

# 29.

# EXTRACTIVE METALLURGY

## 1. OCCURRENCE OF METALS

The earth's crust is the largest source of metals, besides some soluble salts of metals found in sea water. The mode of occurrence of a metal is largely dependent on its chemical nature. Those metals, which are relatively inert, occur in free or native state (i.e. in uncombined state) but most of the metals are reactive and hence are found in a combined state.

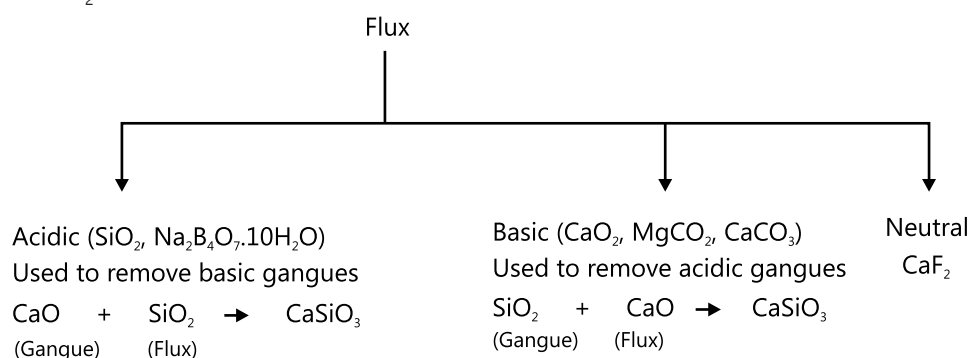
**Mineral:** The compounds of a metal which are naturally available in the earth's crust and can be obtained by mining are called minerals. A mineral may consist of one or more metallic compounds, having almost a fixed composition.

**Ore:** The minerals from which a metal can be extracted economically and conveniently are called ores.

Some important terminologies used in the process are:

**Gangue or Matrix:** Gangue or matrix are the non-metallic impurities present in the ore. In fact, impurities associated with an ore is known as gangue.

**Flux:** Flux are chemical substances which are generally added to an ore in order to remove the impurities or gangue. E.g., CaO, SiO<sub>2</sub> etc.



**Flowchart 29.1:** Classification of flux

**Slag:** Gangue + Flux → Slag

"Slag" is the fusible, light and floatable substance formed due to the reaction between gangue and the flux.

### MASTERJEE CONCEPTS

All ores are minerals but all minerals are not ores.

Vaibhav Krishnan (JEE 2009, AIR 22)

## 2. TYPES OF ORES

Ores may be classified mainly into following 4 classes:-

- (a) **Native ores:** They contain the metal in a free state, and are found in the association of rock or alluvial impurities like clay, sand etc. Silver, gold, platinum etc. occur as native ores. Sometimes, lumps of almost pure metals are also found. These are called nuggets.
- (b) **Oxidized ores:** These ores consist of oxides or oxyalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.

**Table 29.1:** Some important ores of metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < X < 1$ ] $Al_2O_3$
	Diaspore	$Al_2O_3 \cdot H_2O$
	Corundum	$Al_2O_3$
	Kaolinite (a form of clay)	$[Al_2(OH)_4Si_2O_5]$
Iron	Hematite	$Fe_2O_3$
	Magnetite	$Fe_3O_4$
	Siderite	$FeCO_3$
	Iron pyrite	$FeS_2$
	Limonite	$Fe_2O_3 \cdot 3H_2O$
Copper	Copper pyrite	$CuFeS_2$
	Copper glance	$Cu_2S$
	Cuprite	$Cu_2O$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
Zinc	Zinc blende or Sphalerite	$ZnS$
	Calamine	$ZnCO_3$
	Zincite	$ZnO$
Lead	Galena	$PbS$
	Anglesite	$PbSO_4$
	Cerrusite	$PbCO_3$
Magnesium	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$ [ $K_2MgCl_4 \cdot 6H_2O$ ]
	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Epsom salt (Epsomite)	$MgSO_4 \cdot 7H_2O$
	Langbeinite	$K_2Mg_2(SO_4)_3$
Tin	Cassiterite (Tin stone)	$SnO_2$
Silver	Silver glance (Argentite)	$Ag_2S$
	Pyrrargyrite (Ruby Silver)	$Ag_3SbS_3$
	Chlorargyrite (Horn silver)	$AgCl$
	Stefinite	$Ag_2SbS_4$
	Prouisitite	$Ag_2AsS_3$

**Illustration 1:** Which metals are supposed to occur in the native state in nature?

**(JEE MAIN)**

**Sol:** Elements below hydrogen in the electrochemical series like Cu, Ag, Au etc, exist as native ores.

**Illustration 2:** Match the ores listed in column I with their correct chemical formula listed in column II.

**(JEE ADVANCED)**

Column I	Column II
(A) Cassiterite	(p) $\text{FeCO}_3$
(B) Siderite	(q) $\text{SnO}_2$
(C) Cerussite	(r) $\text{PbSO}_4$
(D) Anglesite	(s) $\text{PbCO}_3$

**Sol:**  $\text{SnO}_2$  is called cassiterite or tin stone,  $\text{FeCO}_3$  is called siderite.  $\text{PbCO}_3$  is called cerussite and  $\text{PbSO}_4$  is called anglesite. So correct match is  $A \rightarrow q$ ;  $B \rightarrow p$ ;  $C \rightarrow s$  and  $D \rightarrow r$ .

### 3. PRINCIPAL STEPS IN THE RECOVERY OF A METAL FROM ITS ORE

The isolation and extraction of metals from their ores involve the following major steps:

- Crushing of the ore
- Dressing or concentration of the ore
- Isolation of the crude metal from its ore
- Purification or refining of the metal

#### 3.1 Crushing of the Ore

Ore is first crushed by jaw crushers and ground to a powder (pulverization of the ore) with the help of equipment like ball mills and stamp mills.

#### 3.2 Concentration of the Ore

The removal of unwanted, useless impurities from the ore is called dressing, concentration or benefaction of the ore. It involves several steps, and, selection of these steps depends on the difference in the physical properties of the compound of the metal and that of the gangue. Hence, this process can be carried out by two methods of separation - Physical and Chemical.

##### Physical Methods of separation:

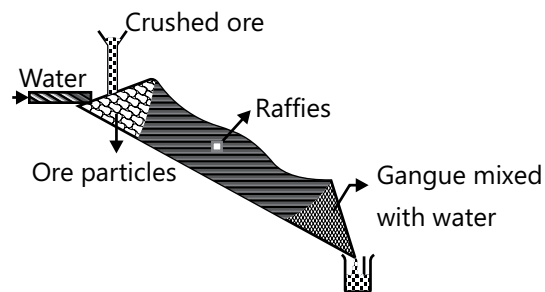
- Gravity separation or levigation
- Magnetic separation
- Froth floatation

Chemical methods of separation, i.e. leaching.

### 3.2.1 Physical Methods of Separation

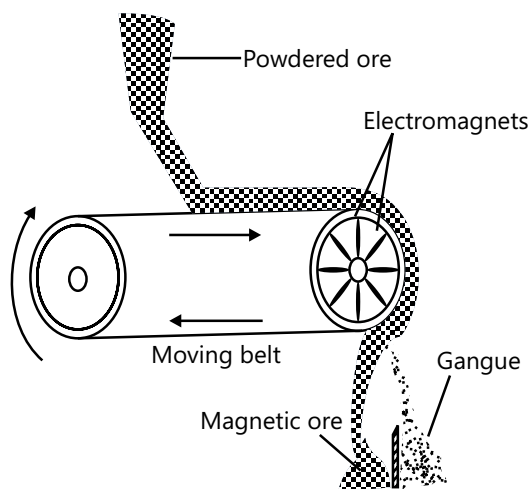
#### Hydraulic Washing/Gravity Separation/ Levigation:

It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with an upward stream of running water. The lighter particles of sand, clay etc. are washed away leaving behind heavier ore particles. For this, either hydraulic classifier or wilfley table is used. This method is generally used for the concentration of oxide and native ores.



**Figure 29.1 :** Representation of gravity separation using wilfley table

**Electromagnetic Separation:** It is based on the differences in magnetic properties of the ore components. It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, the magnetic component of the ore is attracted by the magnetic roller and falls nearer the roller while non-magnetic impurities fall away from it.



**Figure 29.2 :** Electromagnetic separation using Electromagnets

**Examples:** Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is separated from non-magnetic silicious impurities and cassiterite ore ( $\text{SnO}_2$ ) is separated from magnetic Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ).

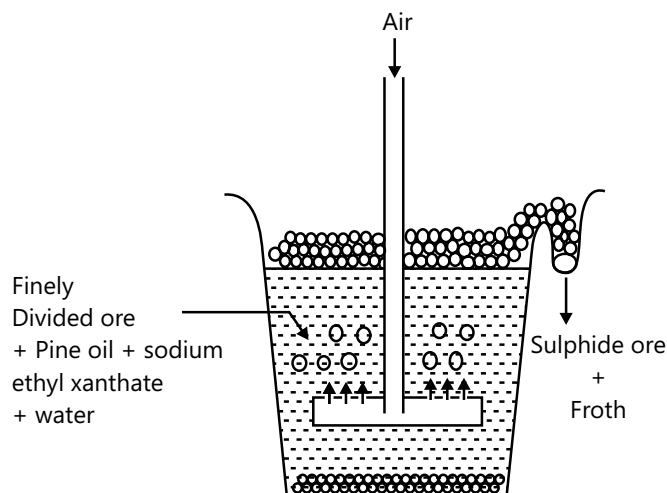
#### MASTERJEE CONCEPTS

- Gravity separation utilizes the difference in density between the ore and the impurity.
- Magnetic separation is used to separate the magnetic impurities/ore from non-magnetic ores/impurities.

**Nikhil Khandelwal (JEE 2009, AIR 94)**

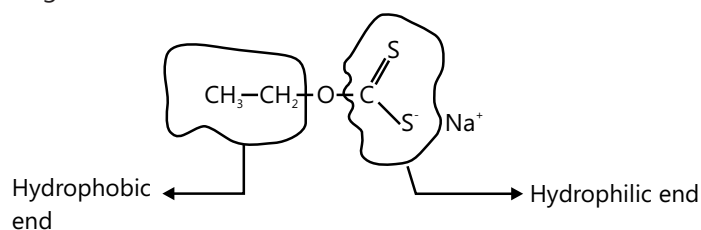
**Froth Floatation Process:** This process is used to separate the sulphide ore from the impurity in the ore. It is based upon the differential wetting of the ore by oil and the impurity by water. In this process, the ore is ground to fine powder and mixed with water to form a slurry mixture. Any one of the oily components, such as pine oil, eucalyptus oil, crude coal tar cresols, etc. is added together with sodium ethyl xanthate as a collector. Air, which acts as an agitator, creates bubbles through the mixture. Finally, the ore is floated to the froth and silicious impurities are settled at the bottom of the tank. Then the froth is collected into a separate container and washed thoroughly and dried. The oil added acts as a frothing agent. It reduces the surface tension of the water and helps to produce

a stable froth. Reagents such as aniline or cresol are used to stabilize the froth. The formation of bubble involves an increase in air-water surface that means doing work against surface tension. The energy required to create a bubble of radius  $r$  is  $2 \times 4 \pi r^2 \times E$ . It is the energy required to create a unit surface area and it is directly proportional to the surface tension. The froth flotation process is usually applied for sulphide ores and the schematic representation is shown in figure. Sodium ethyl xanthate acts as a collector of sulphide ore.



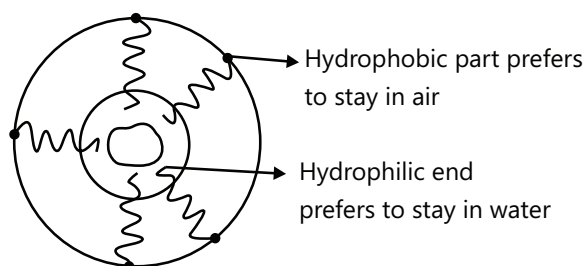
**Figure 29.3:** Froth flotation process for sulphide ore

The hydrophobic end prefers to stay in the air and the hydrophilic end prefers to stay in the water. Since the molecule has both hydrophobic and hydrophilic parts, the best place for it to stay is the air-water interface and hence it exhibits floating characteristics. The hydrophilic end attracts the sulphide particles and forms surface coated particles as shown in figure.



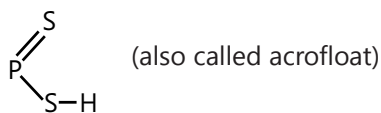
**Figure 29.4-a:** Bonding between dirt particle and sodium ethyl xanthate

Finally, the collected sulphide particles are floated to the froth and transferred to a separate container, washed with huge amounts of water, dried and sent for the next step of extraction.

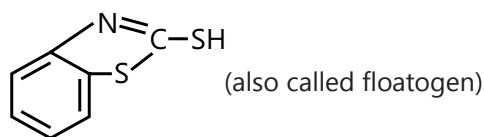


**Figure 29.4-b:** Sodium ethyl xanthate at the air water interface

- (a) The other alkyl groups in xanthate may be amyl ( $C_5H_{11}-$ ), octyl ( $C_8H_{17}-$ ), etc. instead of the ethyl group.
- (b) The other collectors that may be used are;
- (i) Sodium lauryl sulphate :  $C_{12}H_{25}-O-SO_3 Na$
  - (ii) Trimethyl cetly ammonium bromide:  $C_{16}H_{12}N^+(Me)_3Br^-$
  - (iii) Dicesyl dithiophosphate:  $(CH_3-C_6H_4-O)_2$



- (iv) Mecraptobenzthiazole:



The overall ore collecting process occurs through adsorption and depends upon the unbalanced forces on the solid surface.

**Activator** is a substance that is added to help the collector stay attached to the particles to be floated and hence, improves the floating characteristics of the ore. For example, the floating characteristic of ZnS is poor, compared to that of CuS. Hence  $CuSO_4$  is used as an activator to form a coating of CuS on the ZnS surface and improve its floating characteristics.

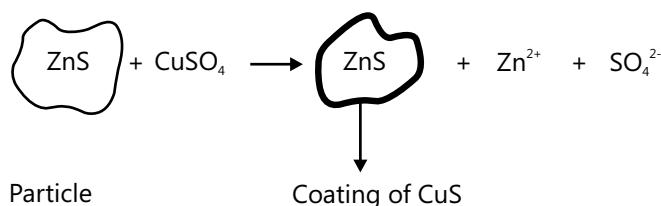


Figure 29.4-c: Action of activator

Accordingly, using suitable activators, the froth flotation process can also be applied for non sulphide ores. For example,  $Na_2S$  is a suitable activator for malachite ( $CuCO_3 \cdot Cu(OH)_2$ ) and anglesite ( $PbSO_4$ ) in which the coatings of CuS and PbS are formed by the activator, respectively.

A depressant is a substance that is added to suppress the floating characteristic of the ore particles. For example, galena (PbS) is associated with another sulphide impurity ZnS, which also rises to the surface with the froth. The reagent NaCN/KCN is used to suppress the floating characteristics of ZnS by forming soluble complex with KCN.



### MASTERJEE CONCEPTS

- Froth floatation is used to separate the sulphide ores from its impurities.
- Froth floatation is based on the principle of differential wetting of the ore by oil and impurities by water.
- Activator is a substance that helps the collector to stay attached to the particles to be floated.
- Depressant is a substance which suppresses the floating characteristic of the ore.

Saurabh Gupta (JEE 2010, AIR 443)

**Illustration 3:** How does NaCN act as a depressant in preventing ZnS from forming the froth? **(JEE MAIN)**

**Sol:** NaCN reacts with ZnS and forms a layer of  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  complex on the surface of ZnS and prevents it from the formation of froth.

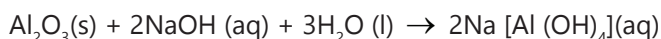
**Illustration 4:** What is the role of a stabilizer in the froth floatation process? **(JEE MAIN)**

**Sol:** Froth can last for a longer period in the presence of a stabilizer.

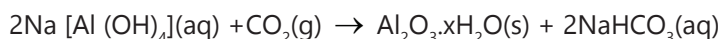
### 3.2.2 Chemical Methods/Leaching

**Leaching:** Leaching is often used if the ore is soluble in some suitable solvent, e.g. acids, bases and suitable chemical reagents.

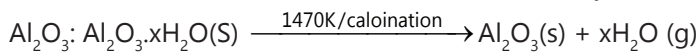
**Leaching of alumina from bauxite:** The principal ore of aluminium, bauxite, usually contains  $\text{SiO}_2$ , iron oxide and titanium oxide ( $\text{TiO}_2$ ) as impurities. The concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473 - 523 K and 35 - 36 bar pressure. This way,  $\text{Al}_2\text{O}_3$  is leached out as sodium aluminate (and also  $\text{SiO}_2$  as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.



The aluminate in solution is neutralised by passing  $\text{CO}_2$  gas and hydrated  $\text{Al}_2\text{O}_3$  is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated  $\text{Al}_2\text{O}_3$  which induces the precipitation.

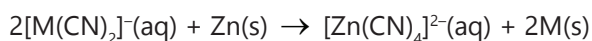


The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure



These steps comprise the Bayer's process.

**Other examples:** In the metallurgy of silver and that of gold, the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or  $\text{O}_2$ ) from which the metal is obtained later by displacement with zinc scrap.



#### MASTERJEE CONCEPTS

Leaching is based on the difference of reactivity of the ore and impurity towards acids and bases.

**Neeraj Toshniwal JEE 2009, AIR 21**

### 3.3 Extraction of Concentrated Ore from Crude Metal

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

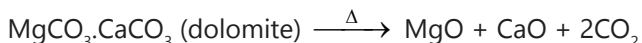
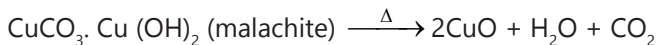
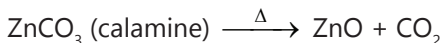
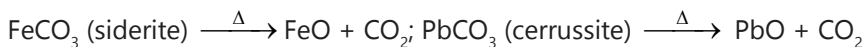
- (i) Conversion to oxide      (ii) Reduction of the oxide to metal

#### 3.3.1 Conversion to Oxide

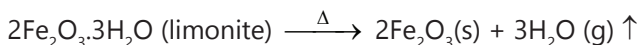
Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

**Calcination:** It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes:

(a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.



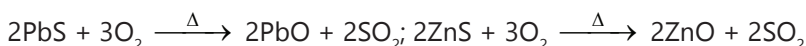
(b) Water of crystallization present in the hydrated oxide ore is lost as moisture, e.g.



(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

**Roasting:** It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or  $\text{O}_2$  below its melting point. Roasting is an exothermic process; once started, it does not require additional heating. The process of roasting does the following things:

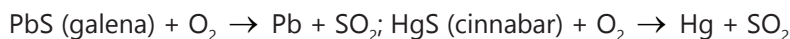
(a) Roasting at moderate temperature: Some portion of the sulphide ores like galena ( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ ) is converted into metallic oxide. If the temperature is fairly low (about  $500^\circ\text{C}$ ) and the concentration of  $\text{SO}_2$  in the gaseous environment is more, sulphate may be produced, that is stable, and high temperature is needed to decompose them.



Sometimes roasting may not bring about complete oxidation.

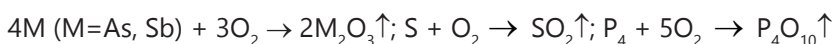


(b) Roasting at high temperature: The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or  $\text{O}_2$  are reduced directly to the metal rather than to the metallic oxides, e.g.  $\text{Cu}_2\text{S}$  (copper glance) +  $\text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2$



The reduction of the sulphide ore directly into metal by heating it in air or  $\text{O}_2$  is known by various names, like self-reduction, auto-reduction, air-reduction etc. The  $\text{SO}_2$  produced is utilized for the manufacture of  $\text{H}_2\text{SO}_4$ .

(c) It removes easily oxidisable volatile impurities like arsenic (as  $\text{As}_2\text{O}_3$ ), sulphur (as  $\text{SO}_2$ ), phosphorus (as  $\text{P}_4\text{O}_{10}$ ) and antimony (as  $\text{Sb}_2\text{O}_3$ ).



These oxides being volatile, escape as gases through the chimney.

(d) When the concentrated tin stone ore  $\text{SnO}_2$  (ore of Sn), is heated strongly in a free supply of air (roasting), the impurities of  $\text{CuS}$  and  $\text{FeS}$  present in the ore are converted into  $\text{CuSO}_4$  and  $\text{FeSO}_4$  respectively



Both calcination and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open, while they are partially or completely closed during calcination.

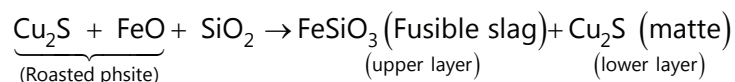
**Slag Formation:** In many extraction processes, an oxide is added deliberately to combine with other impurities to form a stable molten phase immiscible with molten metal, called a slag. The process is termed as smelting.



The principle of slag formation is essentially the following:

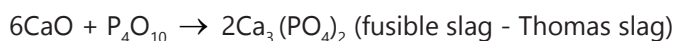
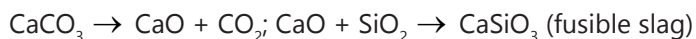
Non metal oxide (acidic oxide) + Metal oxide (basic oxide) → Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in the extraction of Cu from copper pyrite.  $2\text{CuFeS}_2 + 4\text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2$



Matte also contains a very small amount of iron (II) sulphide.

To remove unwanted acidic impurities like sand and  $\text{P}_4\text{O}_{10}$ , smelting is done in the presence of limestone.



### Properties of a Slag:

- Slag is a fusible mass.
- It has a low melting point.
- It is lighter and is immiscible with the molten metal. It is due to these properties that the slag floats as a separate layer on the molten metal and so, can be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised.

**Types of Flux:** Flux are of two types, viz, acidic flux and basic flux.

- Acidic flux:** It is an acidic oxide (oxide of a non-metal) like  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  (from borax). It is used to remove basic impurities like CaO, FeO, MgO etc. The acidic flux combines with a basic impurity to form a slag.
- Basic flux:** It is a basic oxide (i.e. oxide of a metal) like CaO (obtained from lime stone,  $\text{CaCO}_3$ ), MgO (from magnesite,  $\text{MgCO}_3$ ), haematite ( $\text{Fe}_2\text{O}_3$ ) etc. It is used to remove acidic impurities like  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$  etc. The basic flux combines with an acidic impurity to form a slag.

Thus, slag can be defined as a fusible mass, which is obtained when a flux reacts with an infusible, acidic or basic impurity present in the oxide ore.

### MASTERJEE CONCEPTS

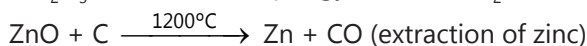
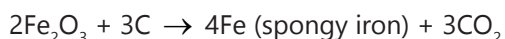
- In Calcination, the concentrated ore is heated to a high temperature in the absence of air.
- In Roasting, the concentrated ore is heated to a high temperature in the presence of air.

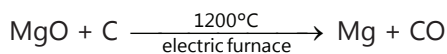
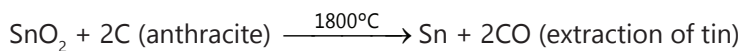
**Aman Gour (JEE 2012, AIR 230)**

### 3.3.2 Reduction of the Oxide to Metal

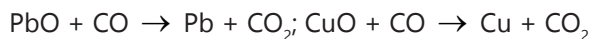
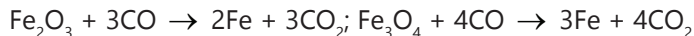
The free metal is obtained by reduction of a compound, using either a chemical reducing agent or by an electrolysis.

**Reduction with Carbon:** A large number of commercial processes come under this category. 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, high temperature is needed, which is expensive and necessitates the use of the blast furnace.





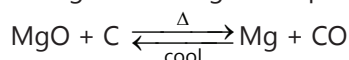
**Reduction with CO:** In some cases CO produced in the furnace itself, is used as a reducing agent.



The reduction process of carbon or carbon monoxide is usually carried out in a blast furnace. There are some disadvantages of using carbon as a reducing agent e.g.:

(a) Some metallic oxides like CaO give metallic carbides instead of metals.  $\text{CaO} + 3\text{C} \xrightarrow{\Delta} \text{CaC}_2 + \text{CO}$

(b) During the cooling of the products, in many cases, reformation of the oxide and carbon may take place.

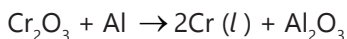


**Reduction by other Metals:** If the temperature needed for carbon to reduce an oxide is too high, for economical or practical purposes, reduction by other metals is done. Also, certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to  $\text{Al}_2\text{O}_3$ . The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.

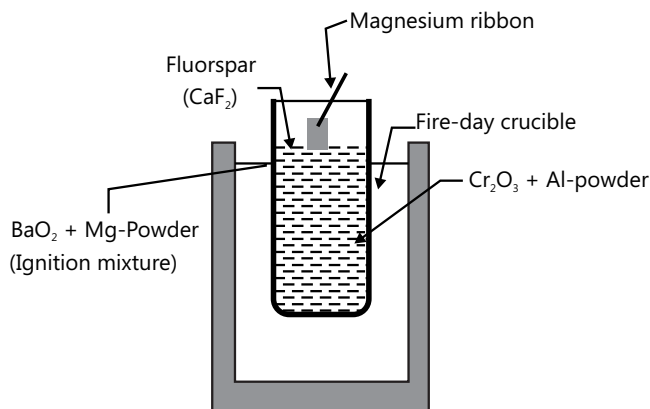
$\text{Cr}_2\text{O}_3$  is mixed with a requisite amount of Al-powder (this mixture is called thermite mixture) and is placed on a large fire-clay crucible. An intimate mixture of  $\text{Na}_2\text{O}_2$  or  $\text{BaO}_2$  and Mg powder (called ignition mixture or igniter) is placed in a small depression made in the thermite mixture. The crucible is surrounded by sand, which prevents the loss of heat by radiation. A piece of Mg ribbon is struck into the ignition mixture and the charge is covered by a layer of fluorspar ( $\text{CaF}_2$ ) which acts as a heat insulator. Now the Mg-ribbon is ignited so that the ignition mixture catches fire and flame is produced, leading to a violent reaction between Mg and  $\text{BaO}_2$  with the evolution of a large amount of heat.



Heat produced in the above reaction makes  $\text{Cr}_2\text{O}_3$  and Al powder to react together.



Molten Cr-metal formed settles down at the bottom of the crucible.



**Figure 29.5:** Reduction of  $\text{Cr}_2\text{O}_3$  by Al-powder (Aluminothermic process)

In this process, thermite mixture consisting of  $\text{Fe}_2\text{O}_3$  and Al-powder in 3: 1 ratio is placed in a funnel-shaped crucible, lined internally with magnesite, with a plug hole at its bottom. The thermite mixture is covered with a mixture of  $\text{BaO}_2$  and Mg-powder (ignition mixture) in which a piece of Mg ribbon is inserted. The ends of the iron pieces to be welded are thoroughly cleaned and surrounded by a fire-clay mould. When the Mg ribbon is ignited, the ignition mixture catches fire and  $\text{Fe}_2\text{O}_3$  gets reduced to Fe by Al-powder.

$2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$  (molten);  $\Delta H = -3230 \text{ kJ}$  (The reaction is used for thermite welding)

$3\text{Mn}_3\text{O}_4 + 8\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 9 \text{Mn}$ ;  $\text{B}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{B} + \text{Al}_2\text{O}_3$  (extraction of boron)

As it is a strongly exothermic reaction, it proceeds with explosive violence and only initial heating is needed.

**Magnesium Reduction Method:** Magnesium is used in a similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.

$\text{TiCl}_4 + 2 \text{Mg} \xrightarrow[1000-1150^\circ\text{C}]{\text{kroll process}} \text{Ti} + 2 \text{MgCl}_2$ ;  $\text{TiCl}_4 + 4\text{Na} \xrightarrow{\text{IMI process}} \text{Ti} + 4\text{NaCl}$

Advantages of using Na and Mg as reducing agents are, the higher reducing power of the metals and solubility of their halides in water, so that the reduced metals can be washed free from impurities.

**Self Reduction method:** This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate. Then that reacts with the remaining part of the sulphide ore to give its metal and  $\text{SO}_2$ .

**Examples:**  $2\text{HgS} + 3\text{O}_2 \rightarrow 2\text{HgO} + 2\text{SO}_2$ ;  $2\text{HgO} + \text{HgS} \rightarrow 3\text{Hg} + \text{SO}_2$

$2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ ;  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$

$2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2 \text{SO}_2$ ;  $2\text{PbO} + \text{PbS} \rightarrow 3\text{Pb} + \text{SO}_2$

The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as

$\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$ ;  $\text{PbSO}_4 + \text{PbS} \rightarrow 2 \text{Pb} + 2\text{SO}_2$

**Electrolytic Reduction Method:** It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals, such as magnesium or aluminum, or for the production of samples of high purity. Electrolytic reduction of copper has the additional advantage of allowing the recovery of valuable minor contaminants such as silver.

- In aqueous solution:** Electrolysis can be carried out conveniently and cheaply in an aqueous solution, so that the products do not react with water. Copper and zinc are obtained by electrolysis of the aqueous solution of their sulphates.
- In other solvents:** Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water and it is produced by electrolysis of  $\text{KHF}_2$  dissolved in anhydrous HF.
- In fused melts:** Elements that react with water are often extracted from fused melts of their ionic salts. Aluminum is obtained by the electrolysis of a fused mixture of  $\text{Al}_2\text{O}_3$  and cryolite  $\text{Na}_3[\text{AlF}_6]$ . Both sodium and chlorine are obtained from the electrolysis of fused NaCl. In this case, upto two-thirds by weight of  $\text{CaCl}_2$  is added as an impurity to lower the melting point from 803 to 505°C.

**Electrochemical Principles of Metallurgy:** Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuits to a reactive or a physical process with a more negative  $\Delta G$ . The free energy available from the external source can be assessed from the potential it produces, across the electrodes, using the thermodynamic relation:

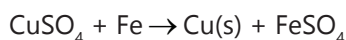
$\Delta G = -nFE \dots$  (i) where,  $n$  is the number of electrons transferred,  $F$  is Faraday's constant ( $F = 96.5 \text{ kJ/mol}$ ) and  $E^\circ$  is the electrode potential of the redox couple, formed in the system.

Hence, the total Gibb's energy of the coupled internal and external process is  $\Delta G + \Delta G_{\text{external}} = \Delta G - nFE_{\text{ext}}$

If the potential difference of the external source exceeds  $E_{\text{ext}} = -\frac{\Delta G}{nF}$  then, the reduction is thermodynamically

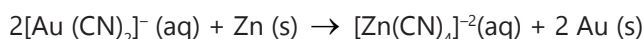
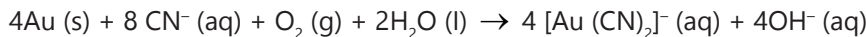
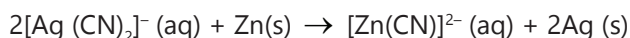
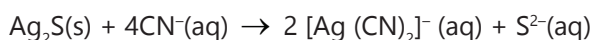
feasible. Thus, the overall process occurs with a decrease in free energy. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two  $E^\circ$  values corresponds to a positive  $E^\circ$  and consequently negative  $\Delta G^\circ$  in equation (i), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,  $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$

**Hydrometallurgy:** The processing of extraction of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing an aqueous solution is known as hydrometallurgy. Occasionally, organic reagents are also used. This method of extraction is generally used for low grade ores. Copper is extracted by hydrometallurgy from a low grade ore. It is leached out using acid and bacteria. The solution containing  $\text{Cu}^{+2}$  is treated with scrap iron or  $\text{H}_2$ .



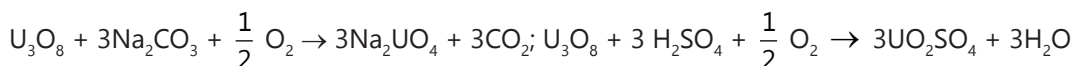
A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching), purification of the leach solution and the subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it. Some of the metals obtained by hydrometallurgy are as follows:

**Extraction of Ag and Au:** Metals like Au and Ag can be precipitated for their salt solution by electropositive metals e.g. Zn. Metallic Ag is dissolved from its ore in a dilute NaCN solution, and the solute so obtained, is treated with scrap Zn when Ag is precipitated. Air is blown into the solution to oxidize  $\text{Na}_2\text{S}$ . Leaching the metals like silver, gold with  $\text{CN}^-$  is an oxidation reaction ( $\text{Ag} \rightarrow \text{Ag}^+$  or  $\text{Au} \rightarrow \text{Au}^+$ )

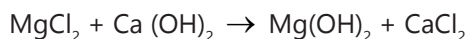


Here Zn acts as a reducing agent.

The leaching pitch blends with  $\text{H}_2\text{SO}_4$  or sodium carbonate to dissolve uranium:



Precipitation of  $\text{Mg}(\text{OH})_2$  from sea water using lime solution:



**Oxidation Reduction:** Besides reductions, some extractions are based on oxidation particularly for non-metals.

(a) A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is found abundantly in sea water as common salt).  $2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$

The  $\Delta G^\circ$  for this reaction is + 422 kJ, when it is converted to  $E^\circ$  (using  $\Delta G^\circ = -nE^\circ F$ ), we get  $E^\circ = -2.2$  V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus,  $\text{Cl}_2$  is obtained by electrolysis giving out  $\text{H}_2$  and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

**Illustration 5:** Common impurities present in Bauxite are:

- (A) CuO      (B) ZnO      (C)  $\text{Fe}_2\text{O}_2$       (D)  $\text{SiO}_2$

**(JEE ADVANCED)**

**Sol:** (C) Red Bauxite contains  $\text{Fe}_2\text{O}_3$  as impurity.

(D) White Bauxite contains  $\text{SiO}_2$  as impurity

**Illustration 6:** Which metals are generally extracted by the electrolytic reduction and why?

**(JEE MAIN)**

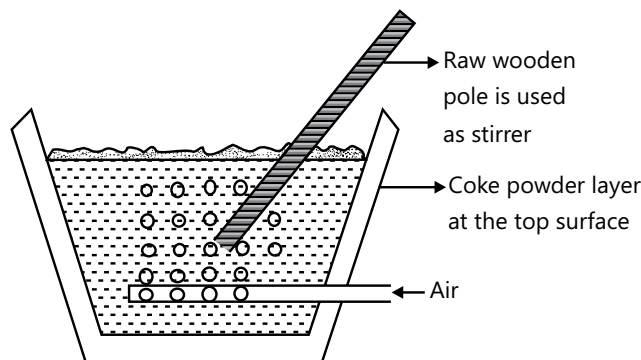
**Sol:** More reactive and electropositive elements acts as strong reducing agents like. Sodium, aluminium, magnesium etc. Hence they cannot be extracted by any of the chemical methods.

### 3.4 Purification or Refining of Metal

Metals obtained by any of the above mentioned reduction processes are not pure and require further refining. There are two methods for the refining of crude metals - Thermal refining and Electro refining.

#### 3.4.1 Thermal Refining

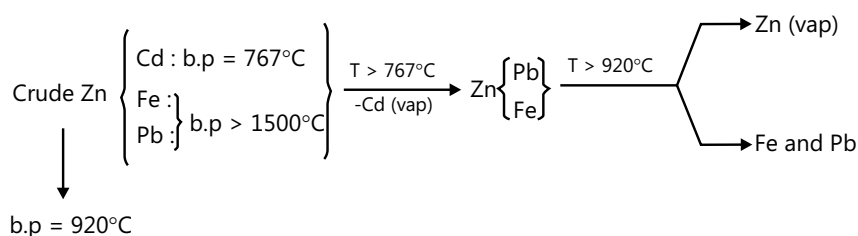
**Oxidation by Air and Poling:** This process is applicable for refining of Cu and Sn. In this process, the crude metal is melted and air is blasted through the melt. After air is blown, the melt is stirred with a raw wooden pole and its unburnt condition produces sufficient amount of carbon and CO to reduce the metallic oxide formed and yield a refined metal. A coke powder layer is maintained at the top of the surface to prevent reoxidation of the metal formed (figure). A small amount of metal to be refined, however, may get oxidized in this process.



**Figure 29.6:** Diagrammatic representation of oxidation by air and poling

The more basic metallic impurities are preferably oxidized by oxygen or air, forming volatile or nonvolatile oxides (i.e. scum). The less basic impurities (if any) are not removed by oxidation, because under this situation, metal to be refined will be oxidized in preference.

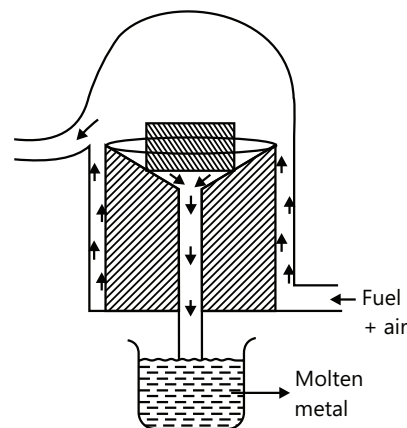
**Fractional Distillation:** This refining process utilizes the boiling point difference between the metal and that of the impurity. Using this process, crude zinc containing Cd, Fe and Pb as impurities can be refined as follows:



At a temperature  $>767^\circ\text{C}$ , Cd separates as vapour; and at temperature  $>920^\circ\text{C}$ , pure Zn separates as vapour, leaving behind Fe and Pb impurities in the melt.

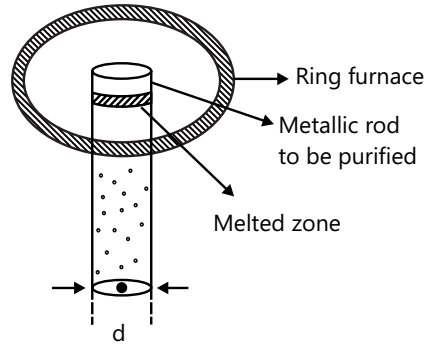
**Liquation:** This method is applicable for metals, such as Sn, Pb and Bi, which have low melting points as compared to their impurities. In this method, the block of crude metal is kept at the top of the sloping furnace and heated just above the melting point of the metal to be refined. The pure metal melts and flows down the sloping hearth and gets collected in a receiver at the bottom of the slope (figure). The perforated block of impurity is thrown later.

The impurity content has to be high enough in the crude metal, otherwise the impurities also flow down with the molten metal.



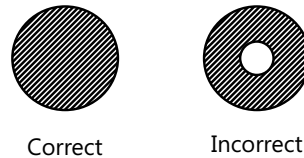
**Figure 29.7:** Diagrammatic representation for liquation

**Zone Refining:** Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultra-purification, because it results in the impurity level decreasing to ppm level. Zone refining is based upon fractional crystallization, as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod (figure (a)), producing a thin zone throughout the cross-sectional area as shown in Figure (b). It is desirable that the diameter of the rod,  $d$ , is small enough to give a uniform melt.

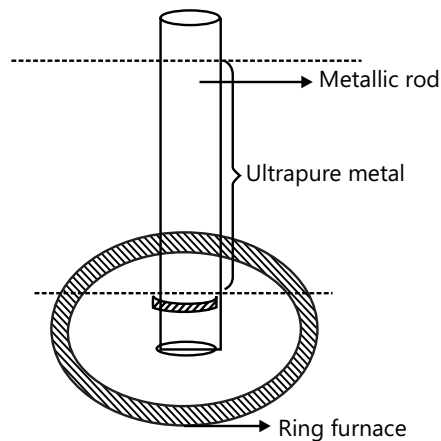


**Figure 29.8-a:** Metal rod heated by ring furnace

When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly, together with the melted zone (figure (c)). The furnace is then switched off, cooled down and taken to the top again for a repetition of the process. Almost all the impurity sweeps out to the bottom after several repetitions of the process.



**Figure 29.8-b:** Cross-sectional view of the metal rod



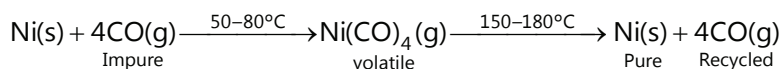
**Figure 29.8-c:** Ring furnace moving down the metal rod

**Vapour Phase Refining:** The two essential criteria for the vapour refining process are listed below:

- (a) The intermediate compound formed has to be volatile.
- (b) The intermediate compound formed has to be relatively unstable, i.e. it should decompose on heating at a practically achievable temperature.

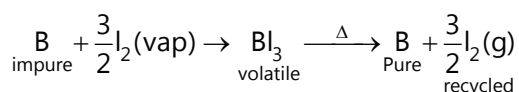
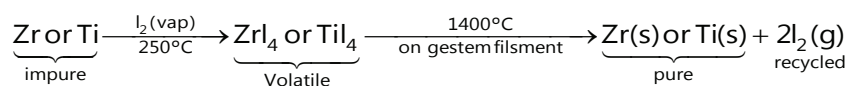
This refining technique is used in the following purification processes:

(i) Mond's process (for purification of nickel):



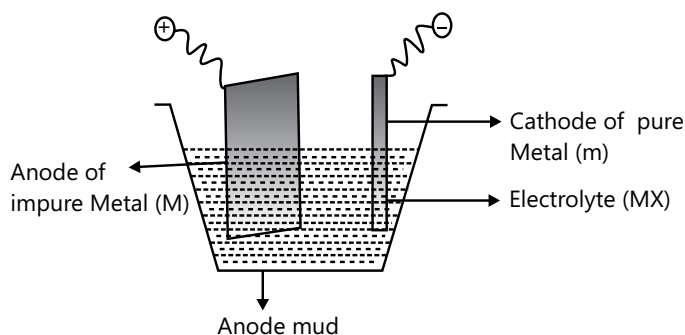
If Ni(CO)<sub>4</sub> is not volatile, it cannot be separated from impurities, so, its volatile nature helps to free it from impurities. Also Ni(CO)<sub>4</sub> needs to undergo thermal decomposition easily, otherwise it cannot produce any pure metal.

(ii) Van-Arkel-de Boer process (for purification of zirconium, boron and titanium):



### 3.4.2 Electro Refining

This method is applicable for the purification of Cu, Zn, Sn, Ag, Au, Ni, Pb and Al. The cathode is made of thin strips of pure metal (same as that to be refined) and the anode is made of large slabs of impure metal (to be refined). The electrolyte is the aqueous solution of a suitable salt of the metal (to be refined) or sometimes, the melt of an oxide/salt.



**Figure 29.9:** Diagrammatic representation of electro refining

The metal gets corroded from the anode. Pure metal gets deposited at the cathode and is purified in this way.

**Reactions at the electrodes:** At cathode:  $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$

At anode : (i)  $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$  (wanted) (ii)  $\text{X}^{n-} \rightarrow \frac{1}{2}\text{X}_2 + n\text{e}^-$  (unwanted)

There are two reactions competing at the anode. So the anionic part of the electrolyte is to be chosen in such a way that the reaction (ii) does not take place at the anode.

Hence at a particular moment, the number of moles of metal dissolved in the electrolyte is equal to the number of moles of metal ions deposited at the cathode. The concentration of metal ion in the electrolyte remains the same at a particular time.

The metallic impurities having lower oxidation potential than that of the metal to be refined are separated in the form of anode mud at the bottom. The suitable electrolytes used in general for respective metals are:

Cu: CuSO<sub>4</sub> solution

Sn: SnSO<sub>4</sub> solution

Ni : N<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution

Zn: ZnSO<sub>4</sub> solution

Ag: AgNO<sub>3</sub> solution

Pb: PbSiF<sub>6</sub> solution

Au: AuCl<sub>3</sub> solution

Al: Al<sub>2</sub>O<sub>3</sub> + (Na<sub>2</sub>AlF<sub>6</sub>) melt + BaF<sub>2</sub>

**MASTERJEE CONCEPTS**

- In the Poling process, a wooden pole is used and the hydrocarbons reduce the metal oxide impurities to refined metal.
- Fractional distillation utilizes the difference in the boiling points between the metal and its impurities.
- Liquation is applicable to metals having much lower melting points, as compared to its impurities.
- Zone refining is based upon fractional crystallization, as the impurity prefers to stay in the melt and the pure metal solidifies on cooling.
- Mond's process is used for nickel, as  $\text{Ni}(\text{CO})_4$  is volatile and on high temperature decomposes to give back pure nickel metal.
- Van arkel de boer's process is used for purification of Zr, B and Ti, as their iodides are volatile and on higher temperature gives back the pure metal. Electro refining is used for purification of Cu, Zn, Sn, Ag, Au, Ni, Pb and Al. Anode consists of impure metal and cathode consists of pure metal.

**B Rajiv Reddy (JEE 2012, AIR 11)****4. THERMODYNAMICS OF EXTRACTION: ELLINGHAM DIAGRAM OF A METAL**

The standard electrode reduction potential of metal provides a very good indicator, or, the ease or difficulty of extracting the metal from its compounds. However, since most metals of industrial importance are obtained by the chemical reduction of their oxide, the free energy changes occurring during these processes are of more fundamental importance. Despite the fact that redox reactions do not always reach equilibrium, thermodynamics can at least be used to identify which reactions are feasible. For a spontaneous reaction the change in free energy  $\Delta G$  must be negative,

$$\Delta G = \Delta H - T\Delta S.$$

It is sufficient to consider  $\Delta G$  because it is related to the equilibrium constant through  $\Delta G = -RT \ln K$ .

Here, a negative value of  $\Delta G$  corresponds to  $K > 1$  and, therefore, a favorable reaction. Reaction rates are also relevant, but at a high temperature, reactions are often fast and we can normally assume that any thermodynamically permissible process can occur. The problem of extracting a metal from its ore is essentially concerned with decomposing the oxide of the metal (apart from simple binary compounds such as metal sulfides and chlorides that occur in nature). Most metal ores consist essentially of a metal oxide in association with one or more nonmetal oxides. Ores like carbonates, sulphides etc. are also converted to oxides, prior to reduction.

The free energy of formation,  $\Delta G$  is the standard free energy of the reaction.



$\Delta G$  is the free energy of formation per mole of  $\text{O}_2$  consumed.

If the standard free energy of formation,  $\Delta G$  has a negative sign at a given temperature, then the oxide can be expected to form spontaneously from the metal plus oxygen. If  $\Delta G$  has a positive sign, the oxide will be expected to decompose spontaneously into its elements.

The free energy of formation of an oxide can now be determined, provided we know the entropy of the formation.

$$\Delta G = \Delta H - T\Delta S \quad \dots \text{ (iii)}$$



In reaction (ii) oxygen is used up in the course of the reaction. Gases have a more random structure (less ordered) than liquid or solids. In this reaction, the entropy or randomness decreases, and hence  $\Delta S$  is negative (provided that neither the metal nor its oxide  $M_xO_y$  are vaporized). Thus, if the temperature is raised then  $T\Delta S$  becomes more negative. Since,  $T\Delta S$  is subtracted in equation (ii),  $\Delta G$  becomes less negative. Thus, the change in free energy decreases with increase in temperature. The free energy change that occurs when 1 mol of common reactant (in this case  $O_2$ ) is used, may be plotted graphically against the temperature for a number of reaction of metals to their oxides. This graph is shown in the following figure and is called an Ellingham diagram for oxides. Similar diagrams can be produced for 1 mol of S, giving Ellingham diagram for sulphides and similarly for halides using 1 mol of halogen.

This figure shows a number of oxide plots with slopes defined by  $\Delta G / T = -\Delta S$ . It is noted that the entropy change in reaction (ii) is roughly the same for all metal oxides, provided that the boiling point of neither the metal nor oxide is exceeded. Thus, below the boiling point of metal, the slope of all the graphs are roughly the same, since  $T\Delta S$  factor is the same whatever the metal may be. When the temperature is raised, a point will be reached where the graph crosses the  $\Delta G = 0$  line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why  $HgO_3$  for instance, decomposes spontaneously into its elements when heated. Theoretically, all oxides can be decomposed to give metal and oxygen, if a sufficiently high temperature can be attained. In practice, that is easily attainable and these metals can be extracted by thermal decomposition of their oxides. The diagram predicts that MgO and ZnO ought to decompose if heated strongly enough, but it does not hold out much hope for obtaining, say, pure Mg by straight forward heating of the oxide to a high temperature where the boiling point of the metal is exceeded. However the slope increases, since the reaction now involves a larger entropy change as the randomness increases in reactants. For example,  $2Mg(g) + O_2(g) \rightarrow 2MgO(s)$

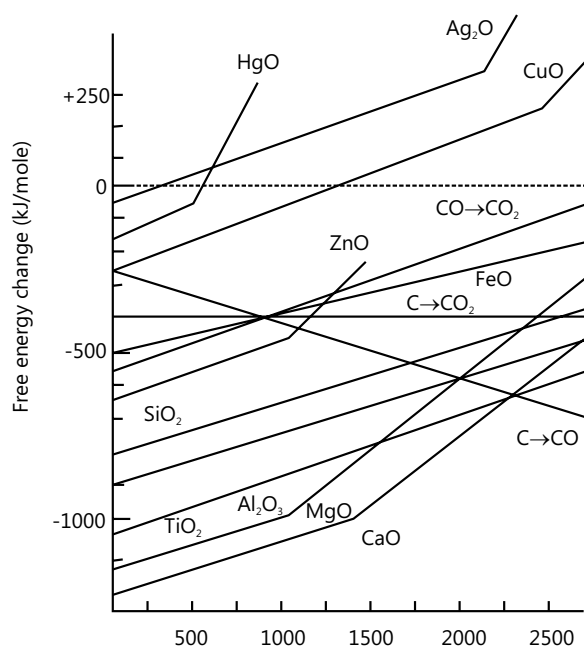


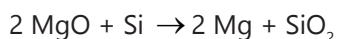
Figure 29.10: Free energy vs temperature  $^{\circ}C$

Here, three moles of gas phases are converted into solid phases in the reaction. This takes place above  $1120^{\circ}C$ , which is the boiling point of Mg. Similarly Hg—HgO line changes slopes at  $365^{\circ}C$ . Several of the plots show abrupt changes in the slopes. These breaks occur at temperatures at which the metal undergoes a phase transition. A smaller effect is seen at the melting point. If, however the oxide undergoes a phase change, there will be an increase in the entropy of the oxide, and at such a point the curve becomes less steep. For example in the case of Pb, the oxide (PbO) boils, while lead is liquid. In these instances the entropy change becomes positive for the reaction and hence the slope  $\Delta G/T$  changes sign, and, the situation reverts to normal once the boiling point of Pb is reached.

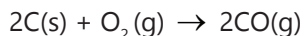
In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second. A vertical line drawn on the Ellingham plot of the metal oxides at any  $T$  gives the sequence of the stabilities of metal oxides. A metal forming a more stable oxide (higher  $-\Delta G$ ) will be the potential reducing agent for a less stable oxide. If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results, but a change of temperature will make the reaction to proceed, provided no kinetic barriers (activation energy) exist. Thus, Mg metal will reduce CuO and FeO, but not CaO. Also, it is seen that at room temperature ( $27^{\circ}C$ ) the order of the reducing ability approximates that of standard electrode potential.

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Although the  $SiO_2$  line is above the MgO line, Si can successfully reduce MgO to free metal. Upto  $1100^{\circ}C$ , the normal boiling point of Mg, the  $\Delta G$  plot for formation of  $SiO_2$  and MgO are parallel. However, above  $1100^{\circ}C$  the plot for MgO changes slope, owing to the increased entropy effect, and above  $1700^{\circ}C$  the reaction between Si and MgO proceeds with decrease in free energy. In practice, the reaction is further enhanced by the distillation of Mg metal from the reaction mixture.



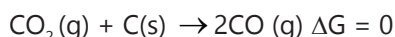
**Carbon/Carbon Monoxide as reducing agent:** In figure, the plot corresponding to the change  $C(s) + O_2(g) \rightarrow CO_2(g)$  is shown by a horizontal line. For this reaction  $\Delta S$  is relatively small because in this case one mole of gaseous product is formed while one mole of gaseous reactant is used up.  $\Delta G$  for this reaction is almost independent of temperature. The plot for  $CO_2$  is relatively high in the figure, and at a lower temperature, C will reduce only a few of the metal oxides as shown. However, the slopes of the plots for several of the metals are such that they cross the  $CO_2$  plot; hence, theoretically these metals can be reduced by C at an elevated temperature. An alternative reaction involving carbon and oxygen is the formation of CO.



Since two gaseous products are formed from one mole of a gaseous reactant, this process is accompanied by an increase in entropy. Hence, the slope of the corresponding line is negative as shown, by the downward sloping line in the figure. If the temperature is high enough, C should reduce all the metal oxides, being converted into CO. The plot for the reaction of CO with oxygen is also shown. There are three curves for carbon, corresponding to complete oxidation of C to  $CO_2$ , partial oxidation to carbon monoxide, and oxidation of CO to carbon dioxide. The three curves pass through a common point at  $710^\circ C$ . Thus, the free energies of formation of  $CO_2$  from carbon monoxide and carbon dioxide from carbon are identical.



Subtracting one equation from the other and rearranging, the following is obtained:



i.e. an equilibrium is set. It is clear, that, below a temperature of  $710^\circ C$ , CO is a more effective reducing agent than carbon, but above this temperature, the reverse is true. All three oxidation curves for the carbon system lie above that for the oxidation of zinc, until a temperature of approximately  $1000^\circ C$  is reached. At this point, carbon is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn ( $907^\circ C$ ), it will be formed as a vapour. The overall equation for reduction is  $ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$

It is interesting to note that the value of carbon as a reducing agent is due to a marked increase in disorder that takes place when carbon (an ordered solid) reacts with one mole of oxygen to give two moles of CO. The net effect is an extra mole of gas and hence an increase in disorder (an increase in entropy). It is a fact, that, in the region of  $2000^\circ C$ , carbon is thermodynamically capable of reducing most metal oxides to metal. Thus, for most metal oxides, a reducing agent is required and we should consider the overall reaction obtained by subtracting the metal oxidation from one carbon oxidation as

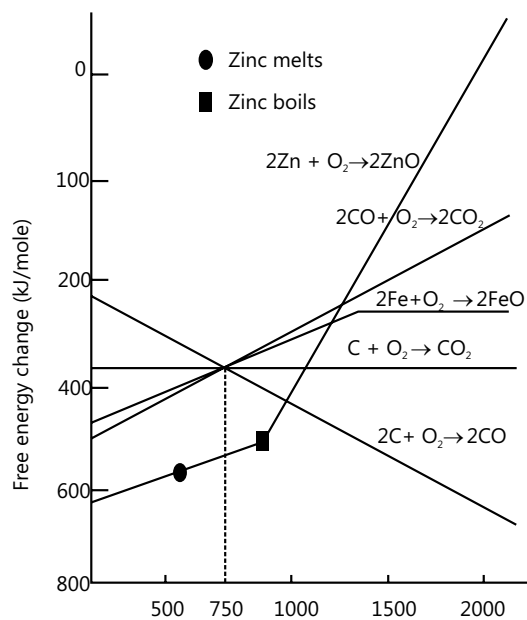


Figure 29.11: Free energy vs temperature  $^\circ C$

$$\Delta G_{\text{overall}} = \Delta G_{(O)} - \Delta G_{(M)}$$

**Metals as reducing agents:** Metal oxide reduction is thermodynamically favorable for temperatures at which the line for the metal oxide is above any one of the lines for carbon oxidation. The  $\Delta G$  for metal oxide reduction by carbon is negative.

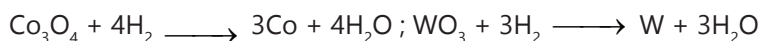
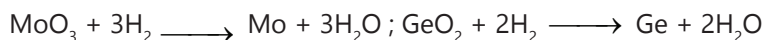
**Note:** The Gibb's energies of formation of most sulphides are greater than that for  $\text{CS}_2$ . In fact,  $\text{CS}_2$  is an endothermic compound. Therefore, the  $\Delta_f G^\circ$  of  $\text{M}_x\text{S}$  is not compensated. So reduction of  $\text{M}_x\text{S}$  is difficult. Hence, it is common practice to roast sulphide ores to corresponding oxides prior to reduction. Similar principles apply to other types of reduction. For instance, if the plot of  $\Delta G_{(M)}$  lies above  $\Delta G_{(M')}$ , M' is now taking the place of C. When  $\Delta G = \Delta G_{(M')} - \Delta G_{(M)}$  is negative, the reaction is,  $\text{M}'\text{O} + \text{M} \rightarrow \text{M} + \text{M}'\text{O}$

**Hydrogen as a reducing agent:** Hydrogen is not a very effective reducing agent for obtaining metals from their oxides. The reason is that  $\Delta S$  is negative for the reaction:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g})$  as the products are less

3 moles of gas                      2 moles of gas

disordered. The plot of  $\Delta G$  against T therefore rises with temperature, meaning that not many metal oxide plots are intersected.  $\text{H}_2$  will therefore reduce oxides such as Cu(I) oxide and Cu(II) oxide, but not the oxides of Al, Mg, and Ca. Oxides of iron are reduced only with difficulty. In the case of magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ , an equilibrium composition is readily established.

In the case of W, Mo, and Co,  $\Delta G$  is above that of  $\text{H}_2\text{O}$  so that  $\text{H}_2$  can reduce these oxides.



This method is not widely used because many metals react with  $\text{H}_2$  at elevated temperatures.

### MASTERJEE CONCEPTS

- If in Ellingham's diagram, a metal A is placed above metal B then metal A can be reduced by metal B.
- The free energy change increases with temperature because the slope is  $\Delta S$  which is negative.

**Rohit Kumar (JEE 2012, AIR 79)**

**Illustration 7:** The reaction  $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$  ( $\Delta G^\circ = -421 \text{ kJ}$ ) is thermodynamically feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature? **(JEE MAIN)**

**Sol:** Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

**Illustration 8:** Is it true, that under certain conditions, Mg can reduce  $\text{Al}_2\text{O}_3$  and Al can reduce MgO? What are those conditions? **(JEE MAIN)**

**Sol:** Below  $1350^\circ\text{C}$ , Mg can reduce  $\text{Al}_2\text{O}_3$  and above  $1350^\circ\text{C}$ , Al can reduce MgO, as evident from the Ellingham diagram.

## 5. METALLURGY OF SOME IMPORTANT METALS

### 5.1 Extraction of Silver

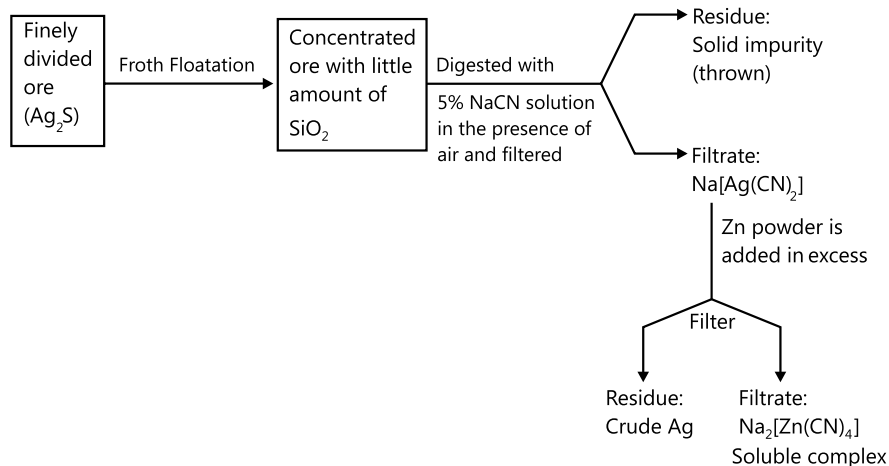
Important ores of silver are

(a) Argentite or silver glance:  $\text{Ag}_2\text{S}$

(b) Ruby silver:  $\text{Ag}_3\text{SbS}_3$

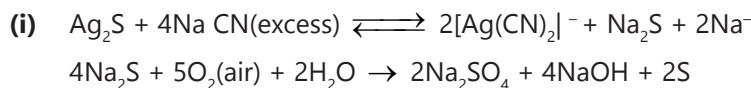
(c) Horn silver:  $\text{AgCl}$

There are three processes commonly used for the extraction of Ag; The cyanide process is described below. The other two processes, i.e. Parke's process and Pattinson's process are beyond the scope of discussion. Cyanide process or Mc-Arthur Forest Process: This process is depicted in the flow diagram given in figure.

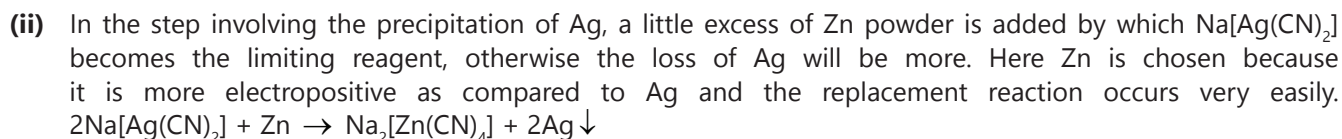


**Flowchart 29.2:** For Mc-Arthur forest for extraction of silver

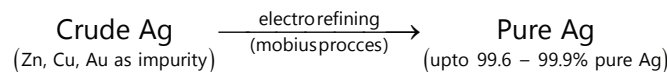
Reactions taking place at the different stages in the cyanide process are as follows:



Since the above reaction is reversible, the conversion ratio is not good. Hence the process is carried out in the presence of air which converts the  $\text{Na}_2\text{S}$  produced into  $\text{Na}_2\text{SO}_4$  and S, and the overall reaction becomes unidirectional.



**Refining of Ag:** Refining of silver is carried out by electrolytic process.



Electrolyte :  $\text{AgNO}_3$  solution + 10%  $\text{HNO}_3$

Cathode : Pure Ag strip

Anode : Impure Ag slab

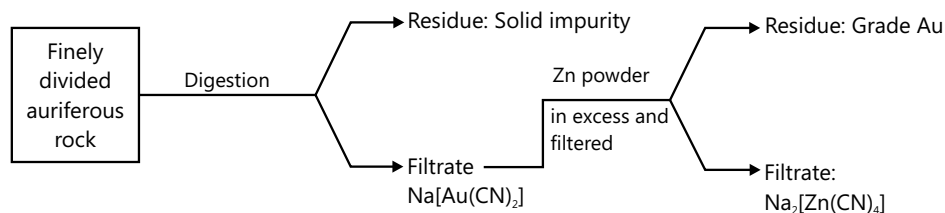
Reactions at the electrodes:

At cathode :  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

At anode :  $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$

## 5.2 Extraction of Gold

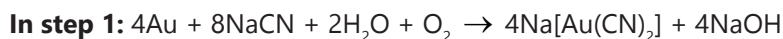
The flow diagram of different stages involved in the cyanide process for extraction of gold is shown in figure.



**Flowchart 29.3:** Cyanide process for extraction of gold

Auriferous rock is rock of quartz contaminated with gold linings.

Reactions taking place in different steps are:



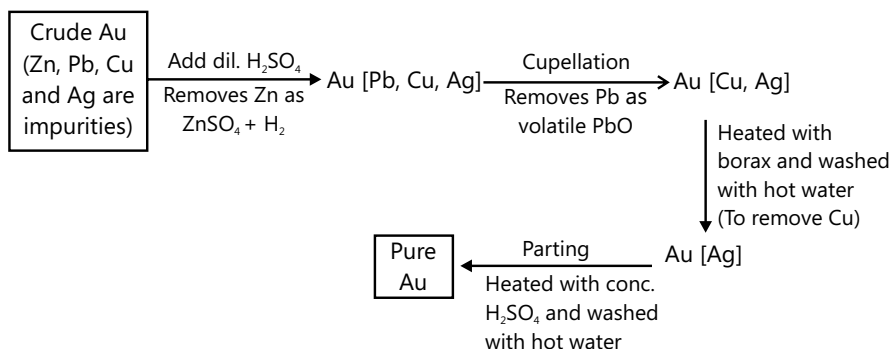
Here, oxidation of Au is not possible without the presence of air and NaCN acts as a complexing agent.



**Refining of Au:** The steps involved in the refining of Au are given in figure. In the third step, on heating with borax, the soluble metaborate of Cu, i.e.  $\text{Cu}(\text{BO}_2)_2$  is formed and washed out with water. Similarly, in the fourth step also, Ag dissolves out as  $\text{Ag}_2\text{SO}_4$  leaving behind pure Au.

**Note:**

- The removal of Ag can also be carried out using chlorine or by electrolysis.
- Cupellation is a process, where crude gold is taken in a small bowl called cupell and melted in the presence of air. Due to the high oxygen affinity of Pb, it is converted into PbO (volatile) which escapes from the system.



**Flowchart 29.4:** Refining of gold

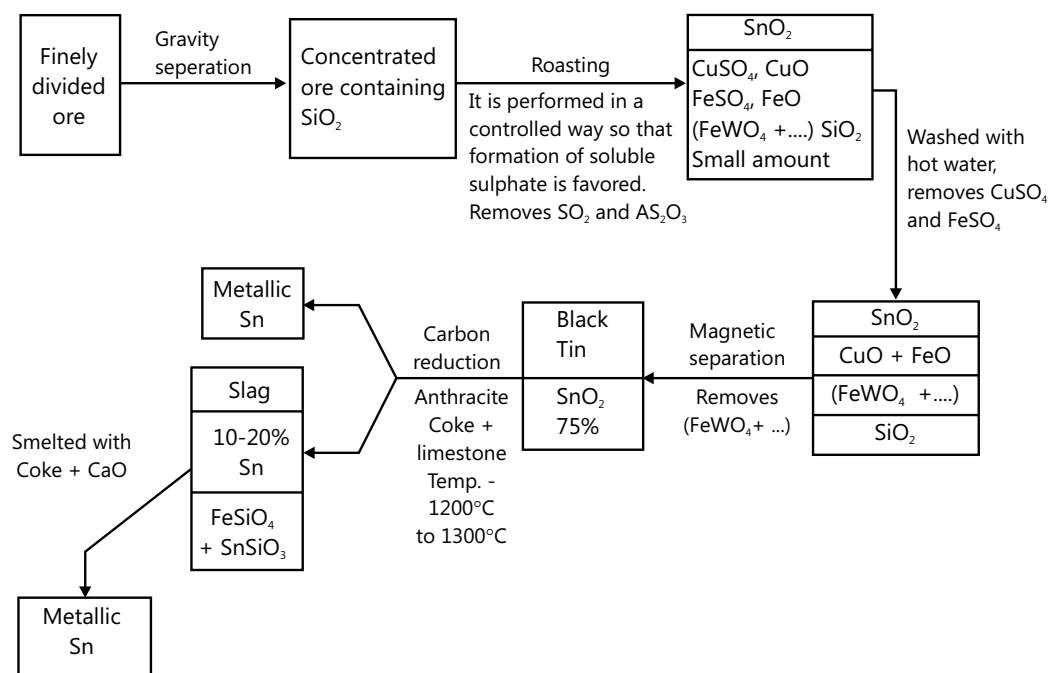
### MASTERJEE CONCEPTS

- Extraction of gold from auriferous rock is done in 2 steps; first it is oxidised by oxygen and treated with NaCN and then it is reduced by zinc.
- During refining, firstly, dilute  $\text{H}_2\text{SO}_4$  removes Zn, then cupellation removes Pb, Cu is removed after heating with borax and washing with water and finally parting's process removes Ag.

**Krishan Mittal (JEE 2012, AIR 199)**

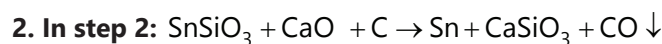
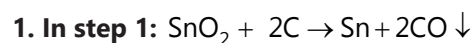
## 5.3 Extraction of Tin

An important ore of tin is cassiterite or tin stone (1-5%  $\text{SnO}_2$  present in it). The main impurities present in the ore are sand ( $\text{SiO}_2$ ), pyrite of Cu and Fe, and wolframite [ $\text{FeWO}_4 + \text{MnWO}_4$ ]. The for extraction of Sn is depicted below.

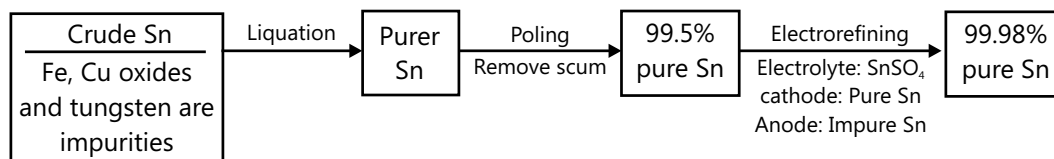


Flowchart 29.5: Extraction of tin

The reactions taking place in the extraction of Sn are:



**Refining of Sn:** The steps involved in the refining of Sn are shown below.



Flowchart 29.6: Refining of tin

### MASTERJEE CONCEPTS

- Extraction of tin involves gravity separation, followed by roasting, followed by magnetic separation and finally carbon reduction. The slag is also smelted.
- In refining, liquation is followed by poling's process and finally by electro refining.

T P Varun (JEE 2012, AIR 64)

## 5.4 Extraction of Magnesium

The important ores of magnesium are:

- Magnesite :  $\text{MgCO}_3$
- Dolomite :  $\text{MgCO}_3 \cdot \text{CaCO}_3$
- Carnallite :  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

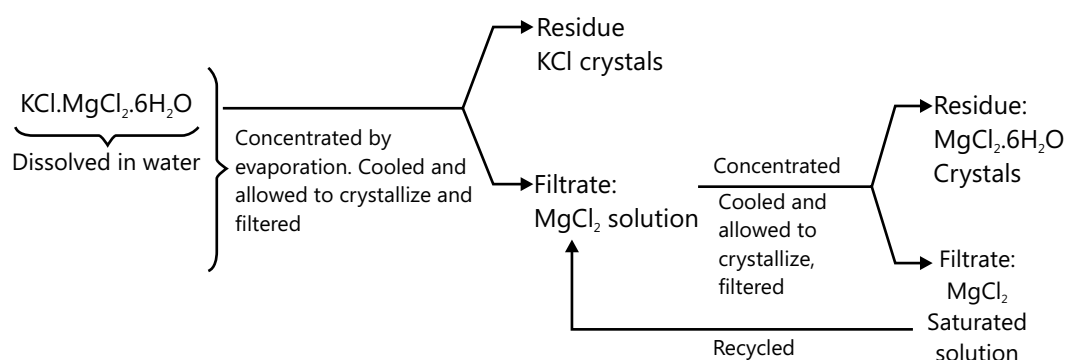
4. Kainite :  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$   
 5. Kieserite :  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$   
 6. Asbestos :  $\text{CaMg}_3(\text{SiO}_3)_4$   
 7. Spinel :  $\text{MgO} \cdot \text{A}_2\text{O}_3$

Two processes recommended for extraction of Mg are electrolytic reduction and carbon reduction. The latter is a very costly process due to very high temperature requirement.

(a) **Electrolytic reduction:** The process for extraction of magnesium consists of the following three steps.

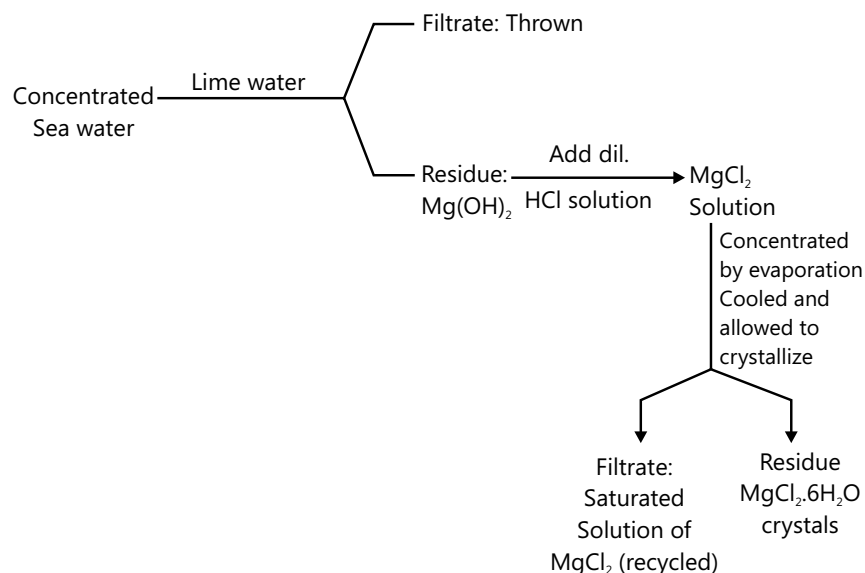
**Step 1: Preparation of hydrated  $\text{MgCl}_2$**

- (i) From Carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ): The steps involved in the preparation of hydrated  $\text{MgCl}_2$  from Carnallite are depicted in figure. The principle behind this process is that KCl is less soluble as compared to  $\text{MgCl}_2$  and crystallizes first.



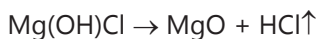
**Flowchart 29.7:** Preparation of hydrated  $\text{MgCl}_2$  from carnallite

- (ii) From sea water: Sea water consists of a lot of  $\text{MgCl}_2$ . The process for extraction of  $\text{MgCl}_2$  from sea water is known as Dow sea water process. The steps involved in the process are depicted in figure. The principle behind this process is that  $\text{Ca}(\text{OH})_2$  is soluble in water while  $\text{Mg}(\text{OH})_2$  is sparingly soluble in water.

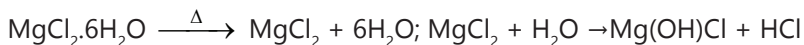


**Flowchart 29.8:** Preparation of hydrated  $\text{MgCl}_2$  from sea water

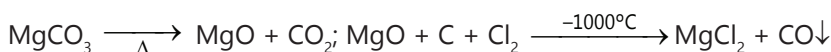
**Step 2: Conversion of hydrated  $\text{MgCl}_2$  to anhydrous  $\text{MgCl}_2$ :** On direct heating of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , anhydrous  $\text{MgCl}_2$  cannot be obtained due to its hydrolysis:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{Mg(OH)Cl} + \text{HCl}\uparrow + 5\text{H}_2\text{O}\uparrow$



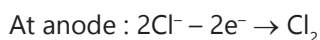
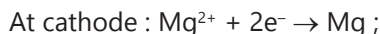
Also,  $\text{MgO}$  formed is an unwanted substance in the electrolytic reduction step due to its very high melting point (i.e.  $2850^\circ\text{C}$ ). Hence hydrated  $\text{MgCl}_2$  is heated to  $175^\circ\text{C}$  in vacuum, in a current of dry  $\text{HCl}$  gas, and  $\text{MgCl}_2$  (anhydrous) is formed.



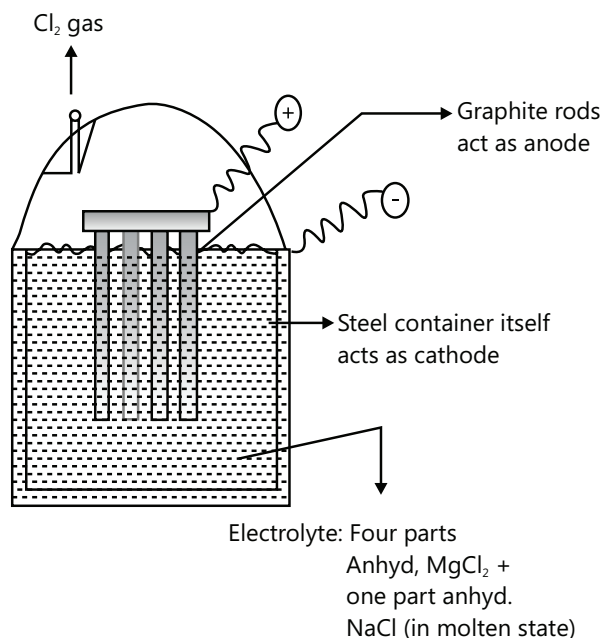
When dry  $\text{HCl}$  is present in the system, the hydrolysis equilibrium shifts towards left but due to increase in thermal energy of the system, the decomposition reaction continues and results in anhydrous  $\text{MgCl}_2$ . An alternative method for preparation of anhydrous  $\text{MgCl}_2$  involves heating calcined magnesite ( $\text{MgO}$ ) to  $1000^\circ\text{C}$  in a current of dry  $\text{Cl}_2$  gas.



**Step 3: Electrolytic reduction of anhydrous  $\text{MgCl}_2$ :** The schematic representation of electrolytic reduction of anhydrous  $\text{MgCl}_2$  is shown in figure:



The container for electrolytic cell has to be covered and the air present inside is removed by passing the coal gas through an opening (not shown in the diagram) to prevent the oxidation of  $\text{Mg}$  formed, which is floating on the top surface of the molten electrolyte.



**Figure 29.12:** Electrolytic reduction of anhydrous  $\text{MgCl}_2$

The electrolyte in the molten state consists of four parts of anhydrous  $\text{MgCl}_2$  and one part anhydrous  $\text{NaCl}$ . One part of  $\text{NaCl}$  is added to reduce the melting temperature of the electrolyte from  $1200^\circ\text{C}$  (m.p. of pure  $\text{MgCl}_2$ ) to  $700^\circ\text{C}$  and at the same time electrical conductivity of the melt is also increased.

Fused carnallite may also be used as an electrolyte because both  $\text{Na}$  and  $\text{K}$  are more electropositive as compared to  $\text{Mg}$  and hence  $\text{Mg}^{2+}$  is preferably discharged at the cathode.



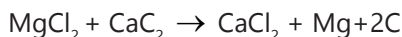
**(b) Carbon reduction process:** In this process for extraction of magnesium, initially MgO is produced from calcination of  $\text{MgCO}_3$ , which is then directly heated with coke powder at around  $2000^\circ\text{C}$  in a closed electric furnace.  $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ ;  $\text{MgO} + \text{C} \rightarrow \text{Mg}\uparrow + \text{CO}\uparrow$

Mg thus obtained comes out in the vapour form and cooled suddenly to about  $200^\circ\text{C}$  by dilution with a large volume of  $\text{H}_2$  gas to prevent reoxidation of Mg.

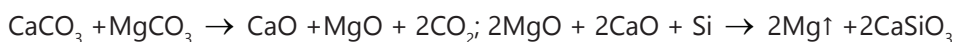
**Note:** Boiling point of Mg is  $-1100^\circ\text{C}$ .

**(c) Other processes:** Some other processes used for extraction of magnesium are:

**(i) Thermal reduction of  $\text{MgCl}_2$ :** The mixture of anhydrous  $\text{MgCl}_2$  and  $\text{CaC}_2$  is heated at  $1500^\circ\text{C}$  and the vapours of Mg are collected in the same way as in the carbon reduction process.



**(ii) Pidgeon process:** Here the calcined mixture of dolomite and powder of ferrosilicon (80% Si) is heated to  $1200^\circ\text{C}$  in a closed container. Mg is vaporized and collected in a condenser.



### MASTERJEE CONCEPTS

Extraction of magnesium involves the following steps - preparation of hydrated  $\text{MgCl}_2$  and conversion of hydrated  $\text{MgCl}_2$  to anhydrous  $\text{MgCl}_2$

**Aishwarya Karnawat (JEE 2012, AIR 839)**

## 5.5 Extraction of Aluminium

The important minerals of Al are:

- Hydrated oxides: Bauxite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) Gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ )  
china clay or Kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ) Diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )
- Oxide : Corundum ( $\text{Al}_2\text{O}_3$ )
- Sulphate : Alunite [ $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$ ]
- Fluoride : Cryolite ( $3\text{NaF} \cdot \text{AlF}_3$ )
- Aluminate : Spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ )
- Silicate : Feldspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ )

Bauxite is the ore most commonly used for extraction of aluminium. Bauxite is of two types:

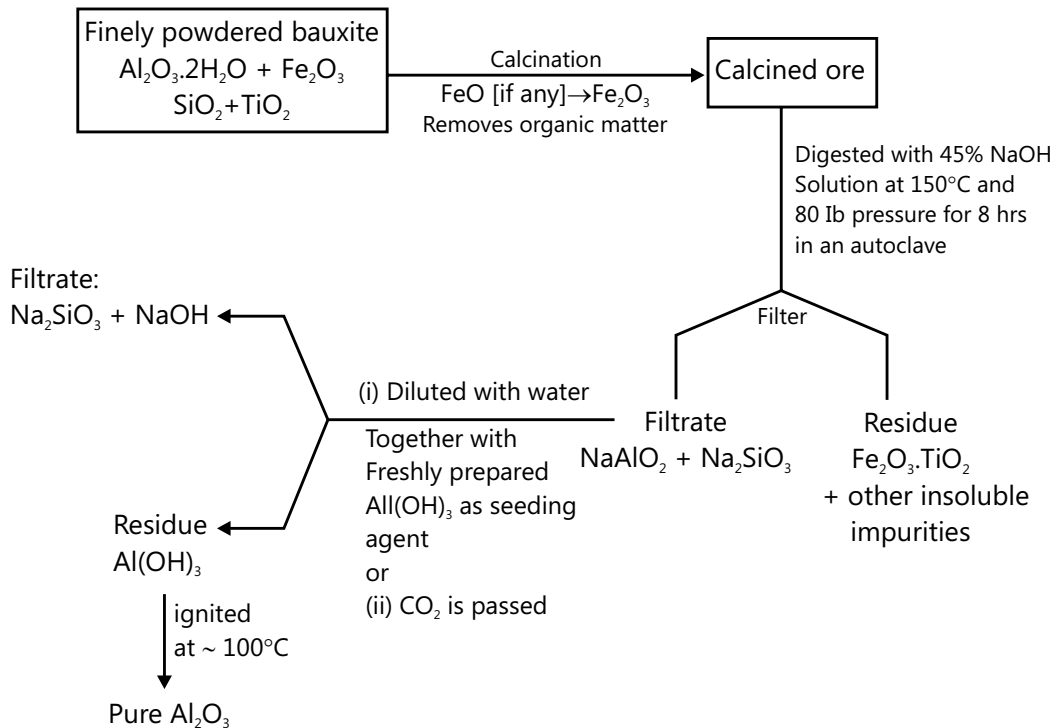
- Red bauxite:  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$  (major impurity) +  $\text{SiO}_2 + \text{TiO}_2$
- White bauxite:  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{SiO}_2$  (major impurity) +  $\text{Fe}_2\text{O}_3 + \text{TiO}_2$

The main steps involved in the extraction of Al from bauxite are:

- Beneficiation of bauxite and preparation of pure alumina.
- Electrolytic reduction of pure alumina.
- Electrorefining of aluminium.

**Beneficiation of bauxite:** Different processes adopted for beneficiation of red and white bauxite are described below.

**Bayer's process:** This is used for beneficiation of red bauxite. Various stages of the process are depicted in the figure.



**Flowchart 29.9:** Bayer's process for beneficiation of bauxite

The reaction involved in the above process are:



**In step 2:**  $[\text{Al}(\text{OH})_4]^- \xrightleftharpoons[\text{OH}^-]{\text{OH}^-} \underset{\text{white}}{\text{Al}(\text{OH})_3} \downarrow \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O}$  Since  $\text{Al}(\text{OH})_3$  is amphoteric in nature, it gets dissolved in alkali as well as in acid as shown in the reactions above. Hence to get  $\text{Al}(\text{OH})_3$  from  $[\text{Al}(\text{OH})_4]^-$ , the pH of the medium is to be reduced, but care has to be taken, that the pH is not low enough to dissolve it further in the form of  $\text{Al}^{3+}$ . The decrease in pH can be done by:-

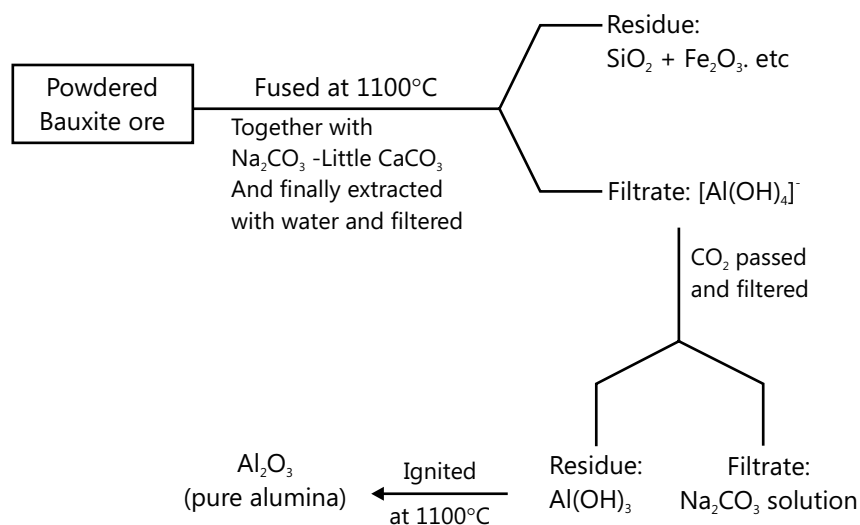
- Adding large amounts of water which increases the volume and decreases the pH. But without the seeding agent (which provides the nucleus of the precipitate) the precipitation is delayed.
- Acidification which reduces the pH of the medium. But here a strong acid is not recommended to avoid any further dissolution of  $\text{Al}(\text{OH})_3$  in the form of  $\text{Al}^{3+}$ . Hence weak acids like  $\text{CO}_2$  gas are passed, which reacts as follows:  $\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$



$\text{OH}^-$  ions are consumed in the above reaction and the formation of  $\text{Al}(\text{OH})_3$  is favoured.

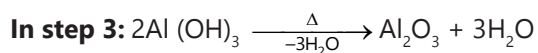
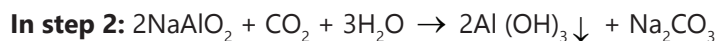
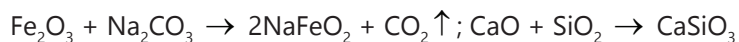
**Note:** The Bayer's process cannot be adopted for white bauxite because the major impurity  $\text{SiO}_2$  is also separated out along with  $\text{Al}_2\text{O}_3$  and finally  $\text{Al}_2\text{O}_3$  of inferior quality is formed.

**Hall's process:** This process is adopted for beneficiation of low grade red bauxite. Various stages of the process are depicted in the flow diagram in Figure.

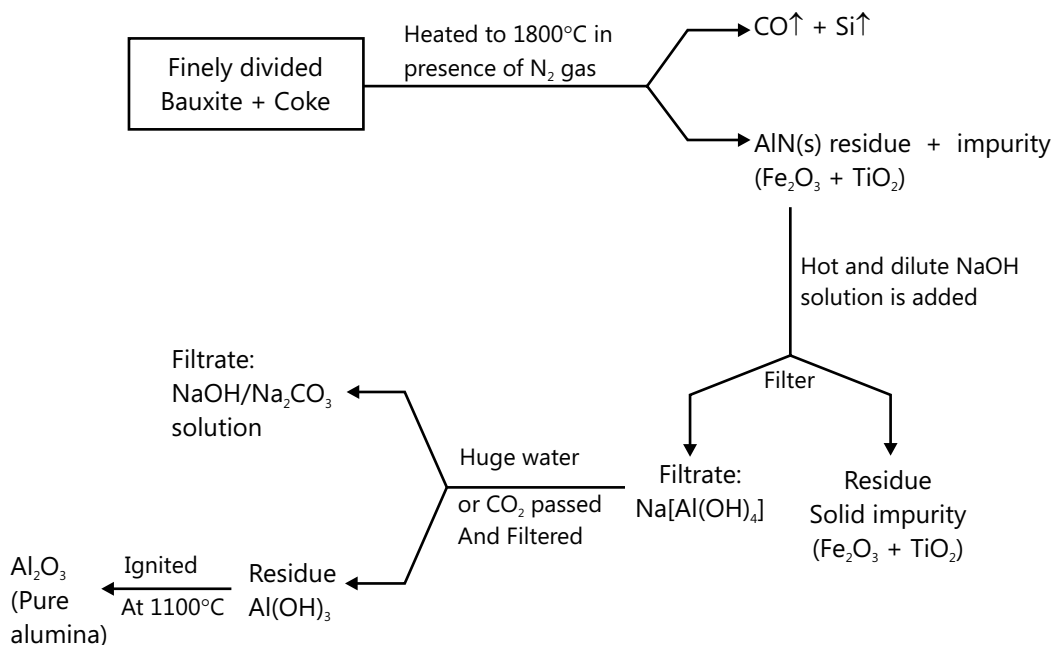


**Flowchart 29.10:** Hall's process for beneficiation of low grade red bauxite

The reactions involved in the above process are:



**Serpeck's process:** This process is used for beneficiation of white bauxite. Various steps of this process are depicted in the flow diagram in figure.



**Flowchart 29.11:** Serpeck's process for beneficiation of white bauxite

The reactions involved in the above process are:

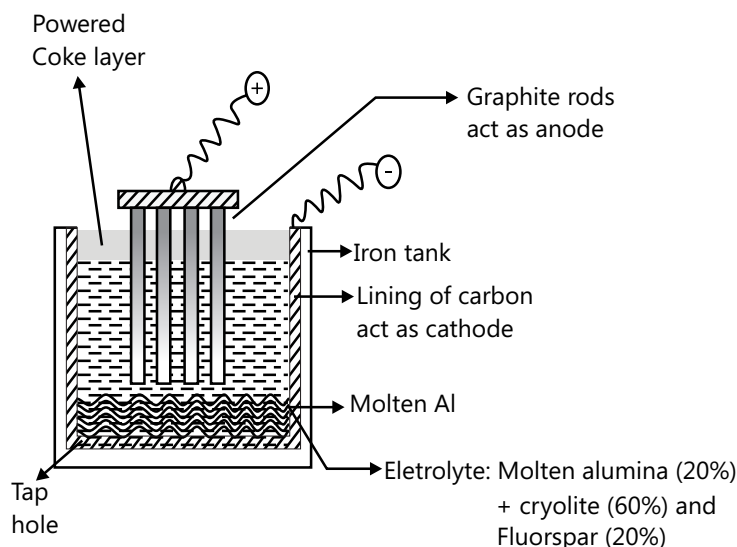
**In step 1:**  $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN}(\text{s}) + 3\text{CO}$ ;  $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} \uparrow + 2\text{CO} \uparrow$

**In step 2:**  $\text{AlN} + \text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{Na}[\text{Al}(\text{OH})_4] + \text{NH}_3 \uparrow$

**In step 3:**  $\text{Na}[\text{Al}(\text{OH})_4] \xrightleftharpoons{\text{H}_2\text{O}} \text{Al}(\text{OH})_3^- + \text{NaOH}$

or  $[\text{Al}(\text{OH})_4]^- \rightleftharpoons \text{Al}(\text{OH})_3 \downarrow + \text{OH}^-$ ;  $\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$

**Electrolytic reduction of pure  $\text{Al}_2\text{O}_3$ :** In the electrolytic reduction of  $\text{Al}_2\text{O}_3$  i.e. molten alumina (20 %) mixed with cryolite (60%) and fluorspar (20 %) is taken in an iron tank with carbon lining that acts as the cathode. A graphite rod hanging from the top acts as the anode. A powdered coke layer is maintained at the top figure.



**Figure 29.13:** Electrolytic reduction of alumina.

On electrolysis, molten Al is deposited at the cathode and since Al is heavier compared to the electrolyte, it gets deposited at the bottom, while oxygen gas is liberated at the anode.

**(a) Reactions**  $\text{Al}_2\text{O}_3 \rightarrow \text{Al}^{3+} + 3\text{O}^{2-}$

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

Since Na and Ca are more electropositive than Al, only  $\text{Al}^{3+}$  gets deposited at the cathode.

At the anode:  $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$

**(b) Functions of fluorspar ( $\text{CaF}_2$ ):** (i) It reduces the melting temperature of the mixture to  $900^\circ\text{C}$  from  $2050^\circ\text{C}$  (Melting point of pure  $\text{Al}_2\text{O}_3$ ) and saves on the fuel cost.

(ii) It also improves the electrical conductivity of the melt, compared to that of molten  $\text{Al}_2\text{O}_3$ .

**(c) Functions of cryolite:** (i) It acts as a solvent and helps dissolve  $\text{Al}_2\text{O}_3$ .

(ii) It also helps to reduce the melting temperature of the mixture.

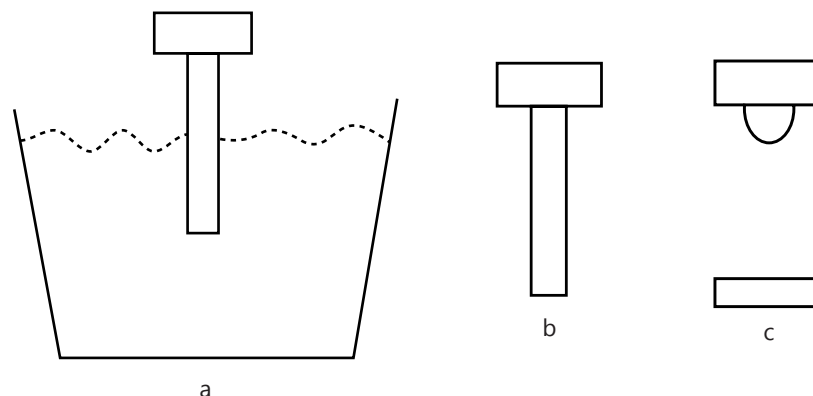
Alternative theory for electrolytic reaction at the anode can explain the dissolution of  $\text{Al}_2\text{O}_3$ .

$\text{AlF}_3 \cdot 3\text{NaF} \rightarrow \text{Al}^{3+} + 3\text{Na}^+ + 6\text{F}^-$ ,  $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$  and  $\text{CaF}_2 \rightarrow \text{Ca}^{2+} + 2\text{F}^-$

Since the  $[\text{F}^-] \gg [\text{O}^{2-}]$ ,  $\text{F}^-$  ions get discharged at the anode first which in turn react with  $\text{Al}_2\text{O}_3$  and liberate  $\text{O}_2$  at the anode.  $2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$ ;  $3\text{F}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{AlF}_3 + \frac{3}{2}\text{O}_2$

**(d) Function of the coke powder layer at the top:** (i) The oxygen liberated at the anode corrodes the anode surface, reacting with graphite to produce CO and  $\text{CO}_2$  and finally the anode cuts down at the bottom and electrical connectivity is lost.

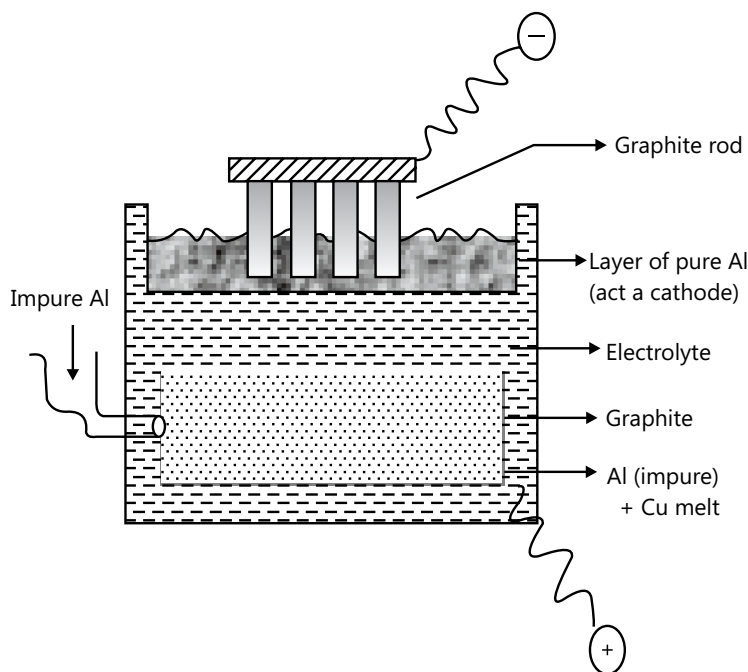
At the junction of liquid-solid-air interface, the energy available is maximum (this can be proved thermodynamically) and corrosion is maximum at this point. To prevent this corrosion, the coke powder (having a large surface area for reaction) layer is kept at the top, which reacts with liberated oxygen.



**Figure 29.14:** Corrosion of graphite anode

(ii) The surface becomes rough unlike the shiny mirror like molten electrolyte; and the radiation loss of heat is also prevented.

**Electro Refining of Aluminium:** Impure aluminium mixed with copper melt is taken in an iron tank with graphite lining. The layer of pure Al acts as the cathode. The graphite rods at the top are essential for electrical connection.



**Figure 29.15:** Electrorefining of aluminium

Here, the electrolyte is the molten mixture of cryolite and  $\text{BaF}_2$  saturated with  $\text{Al}_2\text{O}_3$ .  $\text{BaF}_2$  is added instead of  $\text{CaF}_2$  to adjust the density in such a way that it exists as a separate middle layer. Similarly in impure Al, the Cu melt is deliberately added to increase the density in such a way that it exists as a separate bottom layer.

The reactions involved in the process are: At the anode:  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$

Here, the top surface of bottom layer acts as the anode and Al only enters into the electrolyte as  $\text{Al}^{3+}$  because

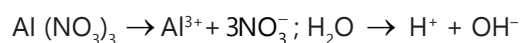
$$E_{\text{Al}^{3+}/\text{Al}}^{\circ} > E_{\text{Cu}/\text{Cu}^{2+}}^{\circ}$$

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

Here, the bottom surface of the top layer (the pure Al melt) acts as the cathode and  $\text{Al}^{3+}$  enters as Al from the electrolyte.

**Note:**

- (a) Impurities like Fe, Si and Cu remain intact in the bottom layer.
- (b) When the thickness of the top layer is increased to a certain limit, it is drained out into a separate container.
- (i) Pure  $\text{Al}_2\text{O}_3$  is not used as the electrolyte because:
- The melting point of  $\text{Al}_2\text{O}_3$  is  $2050^\circ\text{C}$ , hence the power consumption is very high.
  - Al obtained at this temperature gets volatilized and the loss is very high.
  - Aluminium is lighter than  $\text{Al}_2\text{O}_3$  and floats at the top surface and volatilizes easily, as well as attacked by the oxygen, liberated at the anode.
- (ii) The aqueous solution of Al salt cannot be used as an electrolyte because hydrogen is discharged at the cathode in preference to Al, as the discharge potential of  $\text{H}^+$  is smaller compared to  $\text{Al}^{3+}$ . For example, if  $\text{Al}(\text{NO}_3)_3$  is used, then the reactions involved are



**At the cathode:**  $2\text{H}^+ \xrightarrow{+2\text{e}^-} \text{H}_2$

**At the anode:**  $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \uparrow + 4\text{e}^-$

- (b) Molten  $\text{AlCl}_3$  is not chosen as electrolyte because, being covalent in nature, it is a poor conductor of electricity. It also sublimes easily.

### MASTERJEE CONCEPTS

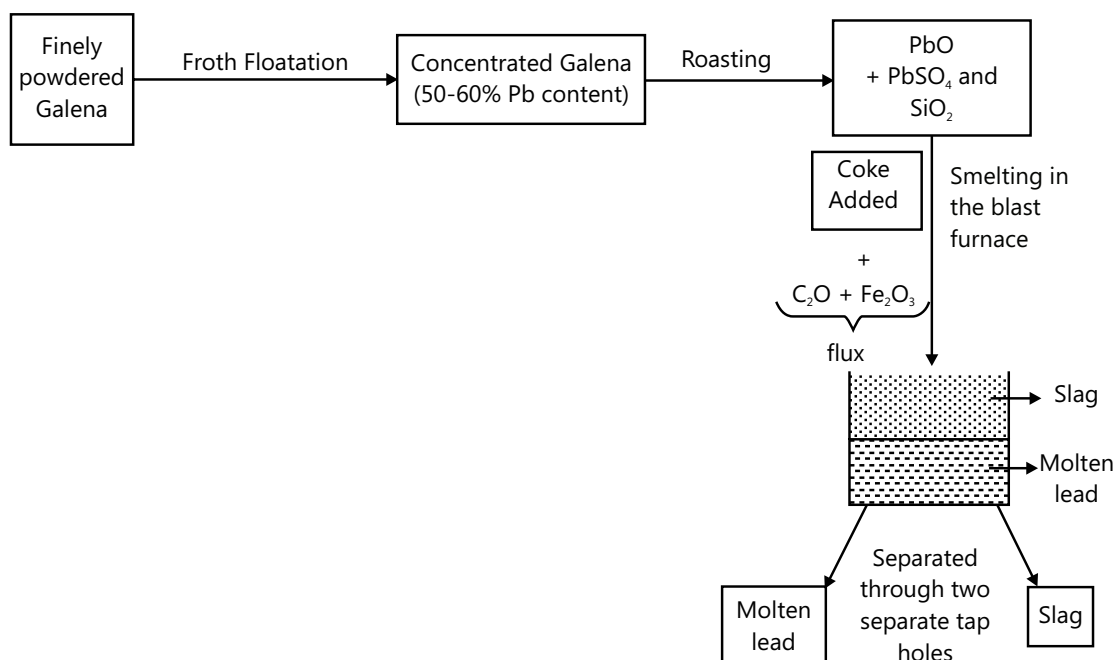
- (a) Main steps involved in the extraction of Al from Bauxite are:
- (i) Beneficiation of bauxite and preparation of pure alumina.
  - (ii) Electrolytic reduction of pure alumina.
  - (iii) Electro refining of aluminium.
- (b) Beneficiation of bauxite includes 3 different processes namely Bayer's process, Hall's process and Serpeck's process, depending on the nature of ore.

**Saurabh Chaterjee (JEE Advanced 2013, AIR)**

## 5.6 Extraction of Lead

The important ores of lead are:

1. Galena :  $\text{PbS}$
2. Cerrusite :  $\text{PbCO}_3$
3. Anglesite :  $\text{PbSO}_4$
4. Crocoisite :  $\text{PbCrO}_4$
5. Lanarkite :  $\text{PbO.PbSO}_4$



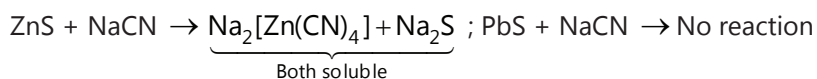
**Flowchart 29.12:** Carbon reduction process for extraction of lead

The ore used commercially for extraction of lead is galena. Depending upon the impurity content, lead can be extracted from galena by one of the following two processes:

- (a) Carbon reduction (when the impurity content is high enough)
- (b) Self-reduction (when the impurity content is low)

The reactions involved at various stages of the process are:

**1. In the froth floatation step:** PbS does not react with NaCN solution while ZnS gets dissolved in NaCN solution and its floating characteristics are completely lost.

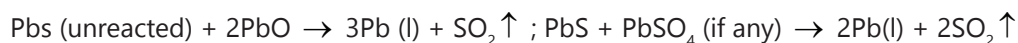
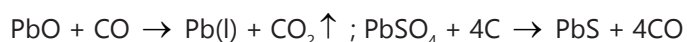
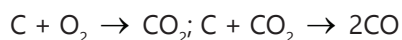


**2. In the roasting step:**  $\text{PbS} + \frac{3}{2}\text{O}_2 \rightarrow \text{PbO} + \text{SO}_2 \uparrow$



Function of lime: Since lime is more basic compared to PbO, CaO reacts preferably with SiO<sub>2</sub> and its presence acts as a negative catalyst towards the formation of PbSiO<sub>3</sub> and PbSO<sub>4</sub>. It also helps to keep the mass porous and helps to complete reaction.

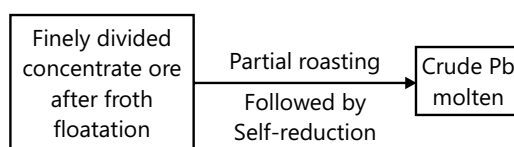
**3. In the smelting step: Initially coke is burnt in a blast of air to produce CO and CO<sub>2</sub>**



**Slag formation reaction:**  $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$



**Self-reduction process:** The steps involved in the self-reduction process are shown in the flow diagram. The reactions involved in the process are:

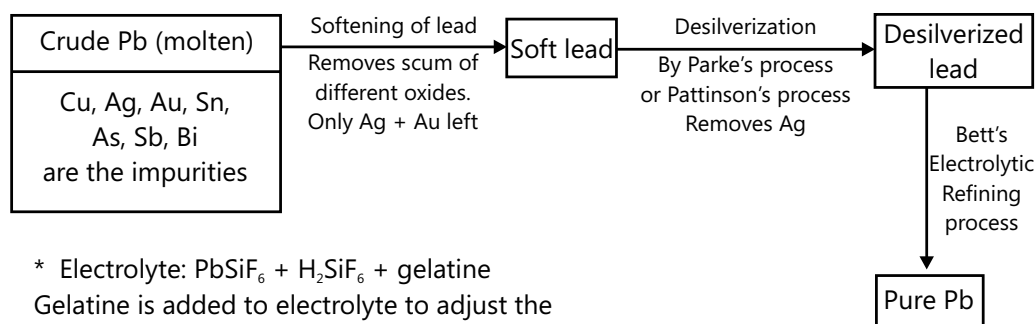


**Flowchart 29.13:** Self-reduction process for extraction of lead

- In the roasting step:  $\text{PbS} + \frac{3}{2}\text{O}_2 \rightarrow \text{PbO} + \text{SO}_2$ ;  $\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$
- In the self-reduction step:  $\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2 \uparrow$ ;  $\text{PbS} + \text{PbSO}_4 \rightarrow 2\text{Pb} + 2\text{SO}_2 \uparrow$

**Note:** After partial roasting, air blasting is stopped and heating is continued for self-reduction reactions.

**Refining of Lead:** The steps for refining of lead are given in the in figure.



\* Electrolyte:  $\text{PbSiF}_6 + \text{H}_2\text{SiF}_6 + \text{gelatine}$   
 Gelatine is added to electrolyte to adjust the viscosity of electrolyte  
 Anode: Impure Pb.  
 Cathode: pure Pb strip

**Flowchart 29.14:** Refining of lead

## MASTERJEE CONCEPTS

- Depending on the impurity content, one of 2 following processes is used:
  - Carbon reduction.
  - Self-reduction.
- Carbon reduction involves froth floatation, roasting and smelting.
- Self reduction involves roasting followed by self-reduction steps.

**Mredul Sharda (JEE Advanced 2013, AIR)**

## 5.7 Extraction of Copper

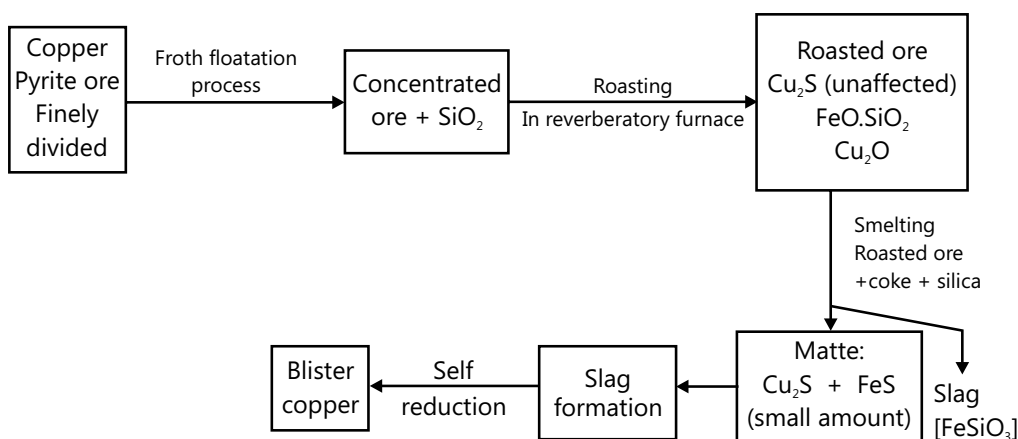
The important ores of Cu are:

- Chalcocite or copper glance :  $\text{Cu}_2\text{S}$
- Copper pyrite or chalcopyrite :  $\text{CuFeS}_2$
- Cuprite or ruby copper :  $\text{Cu}_2\text{O}$
- Malachite :  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
- Azurite :  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$



Less important ores of copper are chrysocolla ( $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$ ) and malonite ( $\text{CuO}$ ).

The chief ore used for extraction of copper is copper pyrite ( $\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{FeS}_2$ ). The flow diagram for extraction of copper from copper pyrite is depicted in figure.

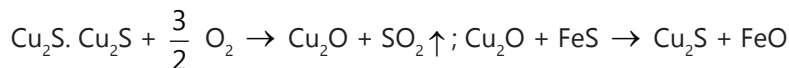


**Flowchart 29.15:** For extraction of copper from copper pyrite

The Changes and reactions involved in the above process are:

- (a) **In the roasting step:** Roasting is done with excess of air and at temperatures below the fusion temperature of the ore,  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2 \uparrow$ ;  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3 + 4\text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2 \uparrow$

Since iron is more electropositive as compared to copper, its sulphide is preferentially oxidized and  $\text{Cu}_2\text{S}$  remains unaffected. If any  $\text{Cu}_2\text{O}$  (little amount) is formed, it also reacts with unreacted  $\text{FeS}$  to give back

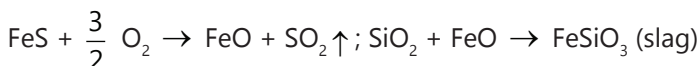


- (b) **In the smelting step:** Coke is used here as fuel to maintain such temperature that keeps the mixture in the molten state.  $\text{FeS} + \frac{3}{2} \text{O}_2 \rightarrow \text{FeO} + \text{SO}_2 \uparrow$



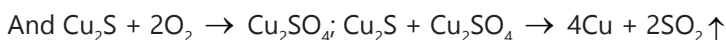
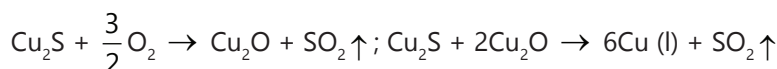
Slag being lighter, floats as an immiscible layer on the top surface of  $\text{Cu}_2\text{S}$  (matte) and is removed through a separate hole.

- (c) **In the Bessemer converter:** The raw material for the Bessemer converter is matte, i.e.  $\text{Cu}_2\text{S} + \text{FeS}$  (little). Here air blasting is initially done for slag formation and  $\text{SiO}_2$  is added from an external source.



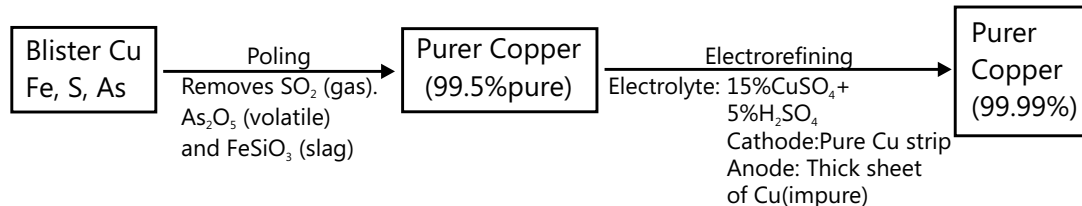
During slag formation, the characteristic green flame is observed at the mouth of the Bessemer converter which indicates the presence of iron in the form of  $\text{FeO}$ . Disappearance of this green flame indicates that the slag formation is complete. Then air blasting is stopped and slag is removed.

Again air blasting is restarted from partial roasting before self-reduction, until two-thirds of  $\text{Cu}_2\text{S}$  is converted into  $\text{Cu}_2\text{O}$ . After this, only heating is continued for the self-reduction process.



Thus the molten  $\text{Cu}$  obtained is poured into a large container and allowed to cool and during cooling, the dissolved  $\text{SO}_2$  comes up to the surface and forms blisters. It is known as blister copper.

**Refining of blister copper:** Blister Cu contains 2-3% impurity (mainly Fe, S and As). The steps involved in its refining are depicted in the flow diagram in figure.



**Flowchart 29.16:** Refining of blister copper

**In the poling step:** The little  $\text{Cu}_2\text{O}$  formed is reduced to metallic Cu by the reducing gases produced from charring of green wooden pole. The powdered anthracite (coke) spread on the top surface of the molten mass also helps to produce a reducing environment.

In the electrorefining step, the impurities like Fe, Ni, Zn get dissolved in the solution, while Au, Ag and Pt are deposited as anode mud below the anode.

### MASTERJEE CONCEPTS

- Extraction of copper includes froth floatation, followed by roasting, then smelting and finally by bessemerization.
- Refining of copper includes poling's process followed by electrorefining.

**Vaibhav Krishnan (JEE 2009, AIR 22)**

## 5.8 Extraction of Zinc

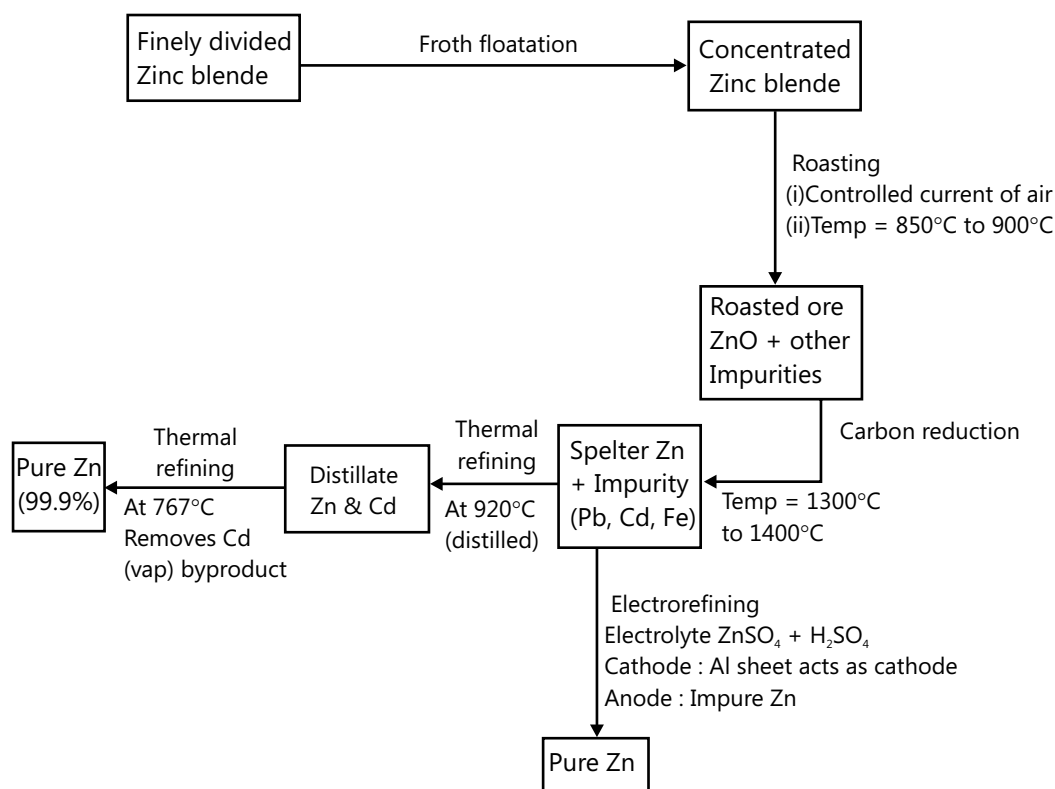
The various ores of zinc are:

1. Zinc blende :  $\text{ZnS}$
2. Zincite :  $\text{ZnO}$
3. Franklinite :  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
4. Calamine :  $\text{ZnCO}_3$
5. Willemite :  $\text{ZnSiO}_3$
6. Electric calamine :  $\text{ZnSiO}_3 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$

The chief ore used for extraction of zinc is zinc blende, which is also known as Black Jack due to the invariable association of galena ( $\text{PbS}$ ) that is black in colour. Sometimes, calamine is also used to extract Zn by carbon reduction process.

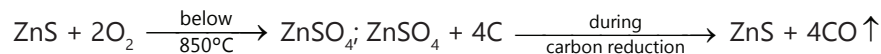
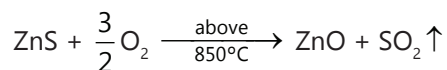
The flow diagram for extraction and refining of zinc from zinc blende is depicted in figure. The changes and reactions involved at various stages of zinc extraction are:

- (a) In the froth floatation step:** This is done in two steps to separate out  $\text{PbS}$  and  $\text{ZnS}$  depending upon their different floating characteristics. On addition of pine oil,  $\text{PbS}$  floats first and is removed. Then more pine oil is added and  $\text{ZnS}$  floats on the top.

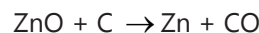


**Flowchart 29.17:** For extraction and refining of zinc from zinc blende

- (b) **In the roasting step:** During roasting, the temperature has to be above  $850^{\circ}\text{C}$  and the air current must be controlled.  $\text{ZnS}$  is converted into  $\text{ZnSO}_4$ , which converts back to  $\text{ZnS}$  during carbon reduction of roasted ore.

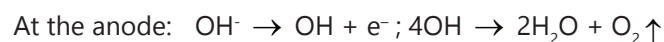
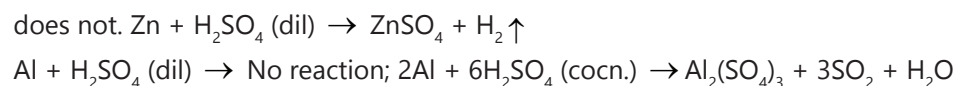


- (c) **In the smelting step:** During smelting, excess coke is used, to stop the production of  $\text{CO}_2$ . Otherwise, Zn reduced will be converted back to  $\text{ZnO}$ . Hence if any  $\text{CO}_2$  is produced, it is allowed to convert into  $\text{CO}$  by the reaction with coke.



The temperature during smelting is kept above  $1300^{\circ}\text{C}$ , though the b.p. of Zn is  $920^{\circ}\text{G}$ . The temperature is kept much higher, compared to that required for vapourizing of zinc in the furnace. This is done because the reaction of carbon dioxide with coke is highly endothermic and brings down the temperature to below  $920^{\circ}\text{C}$  and the evaporation of Zn is affected. Hence, the temperature is maintained at  $1300^{\circ}\text{C}$ - $1400^{\circ}\text{C}$ .

- (d) **In the electrorefining step:** For electrorefining of Zn (crude), Al sheet is used as cathode instead of pure Zn strip. This is because the electrolyte used is  $\text{ZnSO}_4 + \text{H}_2\text{SO}_4$  (dil.), and in dil.  $\text{H}_2\text{SO}_4$ , Zn gets dissolved, while Al does not.  $\text{Zn} + \text{H}_2\text{SO}_4$  (dil)  $\rightarrow \text{ZnSO}_4 + \text{H}_2 \uparrow$



**Note:** The  $\text{H}_2\text{SO}_4$  is added in the electrolyte together with  $\text{ZnSO}_4$  to increase the over voltage of  $\text{H}^+$ . This helps in the deposition of only  $\text{Zn}^{2+}$  at the cathode. Otherwise,  $\text{H}_2$  will be evolved at the cathode.

### MASTERJEE CONCEPTS

Extraction and refining of zinc includes froth floatation, followed by roasting, then smelting and finally refined by either thermal refining or electrorefining.

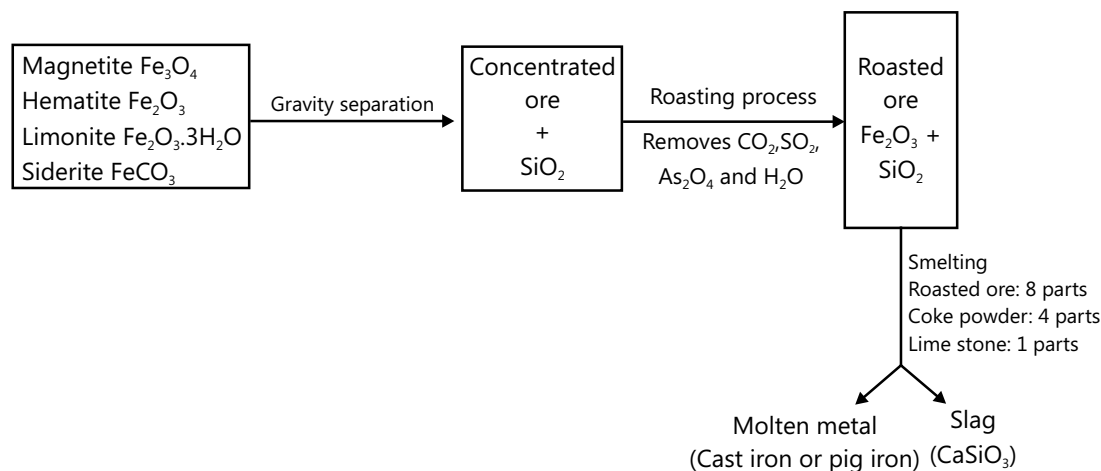
**Nikhil Khandelwal (JEE 2009, AIR 94)**

## 5.9 Extraction of Iron

The various ores of iron are:

1. Hematite :  $\text{Fe}_2\text{O}_3$
2. Magnetite :  $\text{Fe}_3\text{O}_4$
3. Brown hematite or limonite :  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
4. Siderite or spathic iron ore :  $\text{FeCO}_3$
5. Iron pyrite :  $\text{FeS}_2$

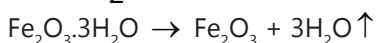
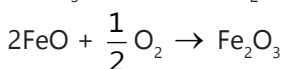
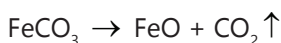
The chief ore used for extraction of iron is hematite, while  $\text{FeS}_2$  is never used because iron obtained from this ore contains a lot of Sulphur, which makes it brittle and useless. The flow diagram for extraction of iron from different ores is depicted in figure.



**Flowchart 29.18:** For extraction of iron from hematite

The reaction at various steps of the iron extraction are:

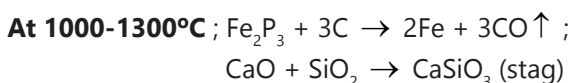
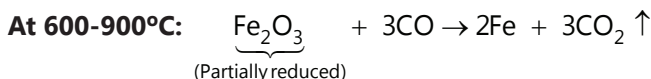
**(a) In the roasting step:**



Hence the final product of roasting is  $\text{Fe}_2\text{O}_3$ . Though there is no sulphide ore yet, roasting is adopted here to convert all FeO present, into  $\text{Fe}_2\text{O}_3$ . As  $\text{Fe}_2\text{O}_3$  does not form slag, this prevents the loss of FeO as slag ( $\text{FeSiO}_3$ ).

- (b) **In the smelting step:** The various changes taking place during smelting in the blast furnace are shown in figure.

The reactions involved are:

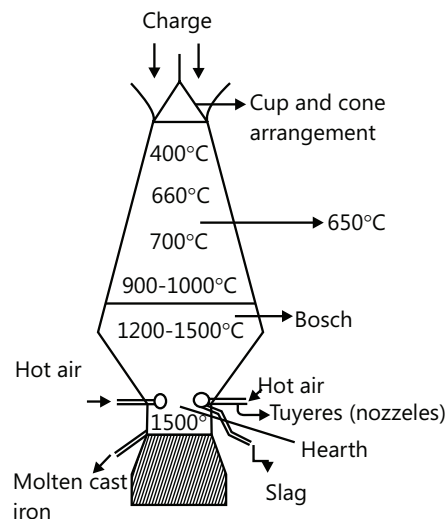


**At 1500°C** (i.e. at the hearth): The coke powder crossing the line of tuyeres does not have the scope of burning anymore and reacts with  $\text{MnO}_2$ ,  $\text{SiO}_2$  to produce impurities like Mn and Si as follows:



$\text{Ca}_3(\text{PO}_4)_2$  present in the limestone reacts with  $\text{SiO}_2$  to produce slag and  $\text{P}_2\text{O}_5$  is reduced by coke to produce  $\text{P}_4$  as impurity:  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 \rightarrow 3\text{CaSiO}_3 + 2\text{P}_2\text{O}_5$ ;  $2\text{P}_4\text{O}_5 + 10\text{C} \rightarrow \text{P}_4 + 10\text{CO} \uparrow$

Finally the cast iron produced consists of impurities like Mn, Si, P, C and S.

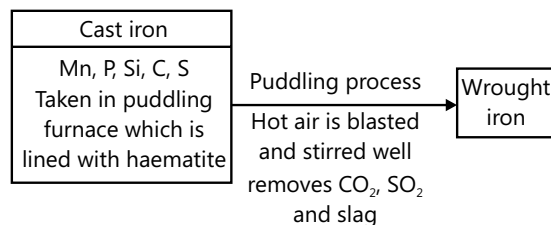
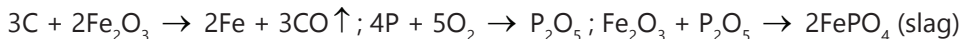
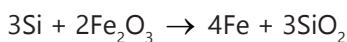
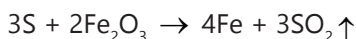


**Figure 29.16:** Smelting in the blast furnace

### Purification of iron or preparation of wrought iron

Wrought iron is the purest form of iron which contains the total impurity less than 0.5%. The carbon content is 0.1 - 0.15% and other impurities (Mn, P, S, Si) are less than 0.3%. The steps involved in preparation of wrought iron are shown in the flow diagram.

The hematite lining has a special significance as it removes the impurity as well as produces iron at that place. The various reactions taking place in the process are:



**Flowchart 29.19:** For preparation of wrought iron from cast iron

### Byproducts of iron extraction

- (a) **Slag:** It consists of huge amounts of  $\text{CaSiO}_3$  and little  $\text{Al}_2(\text{SiO}_3)_3$ . These days it is used for making cement and is now known as slag cement.
- (b) **Blast furnace gas:** The composition of the blast furnace gas is 58%  $\text{N}_2$ , 25%  $\text{CO}$ , 10.5%  $\text{CO}_2$ , 6.5%  $\text{H}_2$  and the rest are hydrocarbons. It contains a very large quantity of  $\text{CO}$  and the  $\text{H}_2$ , which constitutes a good fuel. It is used for preheating the air used and for cooking purposes also.

**Steel Making:** Steel is made by removing most of the carbon and other impurities from pig iron. Composition of various steels depending upon percentage of carbon is given as follows:

%C	Type of steel
0.15-0.3	Mild steel
0.3-0.6	Medium steel

0.6-0.8	High carbon steel
0.8-1.4	Tool steel

The steel making process involves melting and oxidizing C, Si, Mn, S and P present in the pig iron so that these impurities are removed as gases or converted into slag. This is followed by addition of required additives (i.e. different elements) to iron to impart desired properties to steel.

Different elements present in steel provide different properties as described below:

Element	Properties imparted
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P above 0.05%	Imparts low tensile strength and cold brittleness.
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Mn	Imparts high hardness and increases tensile strength, e.g. rail road contains 13% Mn.
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Cr and Ni Imparts stainless characteristics by producing impervious coating of their oxides on the surface.

N (above 0.01%) Makes steel brittle as well as difficult to weld.

C improves hardness and strength.

The addition of mixture of C and Mn into produced steel is known as spiegeleisen. C and Mn act as deoxidizers, remove any dissolved O<sub>2</sub> and reduce FeO (if any). The excess carbon (if any) supplies the desired quality. Mn makes the steel hard and improves its tensile strength also. Various processes used for the preparation of good quality steel are:  $\text{FeO} + \text{Mn} \rightarrow \text{MnO} + \text{Fe}$ ;  $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO} \uparrow$

- Puddling process: This process involves stirring of molten iron in a reverberatory furnace by rods, which are consumed in the process
- Bessemer and Thomas process
- Siemens open hearth process
- Basic oxygen process (also called Linz Donawitz (L.D) process)

All these processes are developed to economize the production of steel from iron. In the Bessemer and Thomas processes, or the Siemens open hearth process, impurities are oxidized by the air, while in the L.D. process, pure O<sub>2</sub> is used for the oxidation of impurities. This is because in the first two processes the molten metal takes up small amounts of nitrogen from the air. In concentrations above 0.01% nitrogen makes steel brittle and nitrating the surface makes the metal more difficult to weld. The use of O<sub>2</sub> not only helps in overcoming these problems but also has the following advantages:

- There is faster conversion, so a given plant can produce more in a day i.e. larger quantities can be handled in lesser time. For example, a 300 tonnes charge can be converted in 40 minutes compared to 6 tonnes in 20 minutes by the Bessemer process.
- It gives a purer product and the surface is free from nitrides.

The lining of the furnace is designed, based on the impurities present in the cast iron:

- If the cast iron contains Mn, but not P, S, Si, then the lining used is silica brick and the process is known as the acid Bessemer process.
- If the cast iron contains acidic impurities such as Si, S, P, a lining of calcined dolomite (CaO.MgO) or magnesia (MgO) is used and the process is called basic Bessemer process. In this process, the P<sub>2</sub>O<sub>3</sub> formed from P combines with lime and forms basic slag [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.CaO], which is known as Thomas slag. It is a valuable byproduct and is sold as phosphate fertilizer.

### Some heat treatment processes related to steel

- Annealing:** The hard steel is heated to bright redness (700-800°C) and then allowed to cool to the room temperature very slowly by which the hard steel becomes soft. This process is known as annealing.
- Quenching or hardening:** The soft steel is heated to bright redness and then cooled suddenly to room temperature immersing it into water or oil, by which the steel becomes hard and brittle. This process is known as quenching.

- (c) **Tempering:** The hard and brittle steel is heated to a 200-300°C temperature range and cooled very slowly to room temperature by which the brittleness of the steel disappears while the hardness remains same. This process is called as tempering.
- (d) **Case-hardening:** For this process the mild steel or wrought iron is heated to bright redness in the presence of hydrocarbons or  $K_4[Fe(CN)_6]$  or heated to bright redness followed by dipping into NaCN/KCN solution. This makes the surface layer hard due to the formation of carbide of Fe (called cementite). This kind of steel is used for making armor plates, cutting tools and machinery parts which are in constant wear and tear.
- (e) **Nitriding:** The mild steel containing 1% Al is heated to 550°C in the presence of  $NH_3$ . This makes the surface layer hard, due to the formation of the nitrides of Fe and Al. This kind of steel is used for making bore well drilling equipment.

### MASTERJEE CONCEPTS

- Extraction of iron includes gravity separation followed by roasting and then smelting to give pig or cast iron.
- Puddling's process is used for purification of iron and converts pig iron to wrought iron.

Saurabh Gupta (JEE 2010, AIR 443)

**Illustration 9:** Auto reduction process issued in extraction of:

- (A) Cu      (B) Hg      (C) Al      (D) Fe

(JEE ADVANCED)

**Sol:** (A) and (B)  $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ ;  $HgS + 2HgO \rightarrow 3Hg + SO_2$

**Illustration 10:** Why is sulphide ore roasted to convert it into the oxide before reduction?

(JEE MAIN)

**Sol:**  $\Delta_f G^\circ$  of most sulphide ores are greater than those of  $CS_2$  and  $H_2S$ . Hence neither carbon nor hydrogen is a suitable reducing agent for the metal sulphides. Moreover the roasting of a sulphide to the oxide is quite advantageous thermodynamically because  $\Delta_f G^\circ$  of oxides are much lower than those of  $SO_2$ .

## POINTS TO REMEMBER

<b>Metallurgy</b>	A collection of processes used for the extraction of metals from their ores which includes its purification and alloy formation
<b>Ore</b>	A mineral from which one or more metals can be extracted easily and profitably.
<b>Flux</b>	A substance used to reduce the m.p. of ore or react with gangue to convert it to slag.
<b>Gangue or matrix</b>	Earthly impurities present with minerals
<b>Pyrometallurgy</b>	Method of thermal reduction (using reducing agent and heat) of ore to metal.
<b>Hydrometallurgy</b>	Method of extraction of metals using leaching and displacement employing cheaper and reactive metal.
<b>Leaching</b>	Method of reacting an ore with some reagent to collect the required metal as water soluble salt.
<b>Smelting</b>	Heating purified oxide form of ore with coke. It may give metal or matte. It is generally known as carbon reduction method.
<b>Aluminothermy</b>	Method of reducing oxide of a metal by heating with powdered aluminium.