

# METALLURGY

## 1. Occurrence of Metals

The earth's crust is the biggest 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 combined state. The naturally occurring inorganic substances, which are obtained by mining, are known as minerals. The mineral has a definite composition. It may be a single compound or a complex mixture. The minerals from which the metals can be conveniently and economically extracted are known as ores. Thus, all ores are minerals, but all minerals are not ores. e.g. cinnabar ( $\text{HgS}$ ) is an ore as well as mineral of mercury but iron pyrites ( $\text{FeS}_2$ ) is a mineral of iron but not an ore. The valuable mineral contained in an ore is an ore mineral. The other minerals contained in the mixture, which ordinary are waste material, constituted the gangue of the ore.

$$\text{Ore} = \text{Ore mineral} + \text{Gangue}$$

The chief ores in the order of economic importance are:

(i) Oxides (ii) sulphides (iii) carbonates (iv) sulphates (v) halides and (vi) silicates.

**(a) Native Ores:** These ores contain metal in free state. For example: Silver, gold, platinum, mercury, copper etc. Sometime lumps of pure metals are found known as *nuggets*.

**(b) Combined Ores:** These ores contain metal in combination with oxygen or sulphur or halides etc. The ores & minerals of various metals are

Metals	Minerals/ores with their chemical formula
1. Iron (VIII, transition metal)	(a) Iron pyrite; $\text{FeS}_2$ (as sulphide) (b) Siderite; $\text{FeCO}_3$ (as carbonate) (c) Red haematite; $\text{Fe}_2\text{O}_3$ (as oxide) (d) Magnetite; $\text{Fe}_3\text{O}_4$ (as oxide) (e) Limonite or brown haematite; $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (as oxide)
2. Copper (IB, coinage metal)	(a) Cuprite; $\text{Cu}_2\text{O}$ (as oxide) (b) Copper pyrites; $\text{CuFeS}_2$ (as sulphides) (c) Copper glance; $\text{Cu}_2\text{S}$ (as sulphides) (d) Malachite; $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (e) Azurite; $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
3. Tin (IV A, amphoteric metal)	(a) Cassiterite or Tin stone; $\text{SnO}_2$ (as oxide) (b) Stannite; $\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{SnS}_2$ (as sulphide)

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| 4. | Lead (IV A, amphoteric metal)       | (a) Galena; $\text{PbS}$ (as sulphide)   |
|    |                                     | (b) Cerussite; $\text{PbCO}_3$ (as carbonate)  |
|    |                                     | (c) Anglessite; $\text{PbSO}_4$ (as sulphate)  |
|    |                                     | (d) White lead; $2\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3$ (as carbonate)   |
| 5. | Magnesium (II A, bridge metal)      | (a) Carnalite; $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (as chloride)                              |
|    |                                     | (b) Dolomite; $\text{MgCO}_3 \cdot \text{CaCO}_3$ (as carbonate)   |
|    |                                     | (c) Magnesite; $\text{MgCO}_3$ (as carbonate)  |
|    |                                     | (d) Epsomite; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (as sulphate)  |
|    |                                     | (e) Kieserite; $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (as sulphate)  |
|    |                                     | (f) Asbestos; $\text{CaMg}(\text{SiO}_3)_4$  |
| 6. | Aluminium (III A, amphoteric metal) | (a) Bauxite; $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (as oxide)  |
|    |                                     | (b) Corundum; $\text{Al}_2\text{O}_3$ (as oxide)   |
|    |                                     | (c) Feldspar; $\text{KAlSi}_3\text{O}_6$ (as oxide)  |
|    |                                     | (d) Clay silicate; $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (as oxide)                  |
|    |                                     | (e) Cryolite; $3\text{NaF} \cdot \text{AlF}_3$ ( $\text{Na}_3\text{AlF}_6$ ) (as halide)                             |
|    |                                     | (f) Alum; $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (as sulphate)          |
|    |                                     | (g) Diaspore; $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (as oxide)  |
|    |                                     | (h) Mica; $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (as oxide) |
| 7. | Zinc (II B, amphoteric metal)       | (a) Zinc blende; $\text{ZnS}$ (as sulphide) or sphalerite  |
|    |                                     | (b) Zincite; $\text{ZnO}$ (as oxide)   |
|    |                                     | (c) Smithsonite, $\text{ZnCO}_3$ (as carbonate)  |
|    |                                     | (d) Hemimorphite or Calamine, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ (as silicate)                       |
| 8. | Silver (IB, best reductive metal)   | (a) Horn silver (chlorapatite); $\text{AgCl}$ (as halide)  |
|    |                                     | (b) Lunar caustic; $\text{AgNO}_3$ (as nitrate)  |
|    |                                     | (c) Silver glance or argentite; $\text{Ag}_2\text{S}$ (as sulphide)  |
|    |                                     | (d) Ruby silver or pyrogyrite; $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$                                    |

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The branch of science that deals with the extraction of metals from their respective ores and the preparation of alloys is called metallurgy. The metallurgy of each metal is an individual problem and the line of treatment depends upon the nature of ore and the chemical properties of the metal. Some common steps involved in the metallurgical operations are

- (i) Crushing and grinding of the ore
- (ii) Concentration or dressing of ore
- (iii) Extraction of crude metal from concentrated ore
- (iv) Reduction of ore to the metallic form and
- (v) Purification of metal

## 2. Crushing and Grinding of the Ore

The ores occur in nature as huge lumps. They are broken to small pieces with the help of crushers. This process is called comminution of ores. Comminution is done in any of the following crushers.

- 1. Jaw crusher 2. Gyratory crusher 3. Symons cone crusher 4. Roll crusher

These pieces are then reduced to fine powder with the help of a ball mill or stamp mill. This process is called pulverisation. Pulverisation is done in any of the following mills.

- 1. Ball mill 2. Rod mill 3. Flint Pebble mill

## 3. Concentration and Dressing of the Ore

The ores obtained from the earth contain large quantities of foreign matter. These unwanted impurities, e.g. earth particles, rocky matter, sand, limestone etc. present in an ore are called gangue or matrix. Prior to the extraction of the metal from the ore, it is necessary to separate, the ore from the gangue. This separation can often be achieved by physical means since mineral and gangue generally occur as separate solid phases. The process of removal of gangue from the ore is technically known as concentration or ore dressing and the purified ore is known as concentrate.

There are various physical and chemical process involved in this step.

### 3.1 Various Processes of Ore Dressing

These processes are cheap and they do not change the chemical composition or state of the ore minerals. Involved processes are given below:

#### Hand Picking

The ore is separated from the main stock in a sufficient degree of purity by simply picking it by hand and then breaking away the adhering rocky materials with a hammer. This is done on the basis of differences in their colour, lustre and lump shape. It may be accomplished on an ore-sorting conveyer.

#### Gravity Separation or Hydraulic Washing (Levigation)

This method of concentration of the ore is based on the difference in specific gravities of the metallic ore and gangue particles. Generally metal ores are heavier than the gangue associated with them. By flowing the powdered ore in a current of water, the lighter rocky impurities can be washed away and the ore particles are

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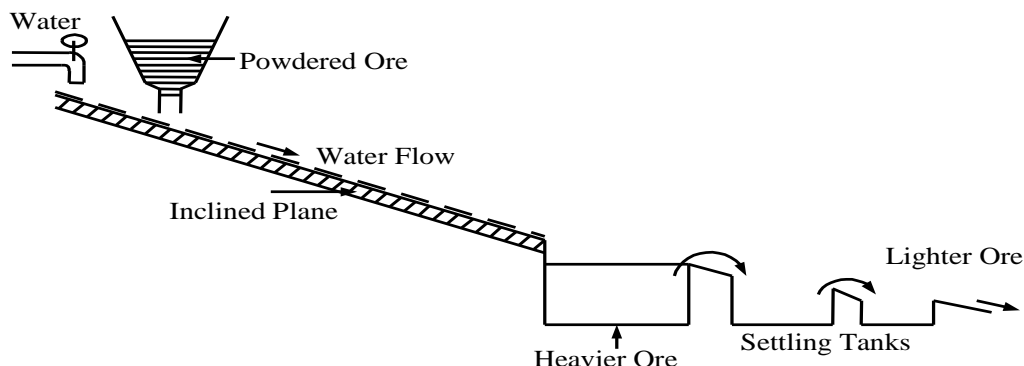
left behind. For this, either wilfley table or Hydraulic classifier is used. Generally oxide and carbonate ores are concentrated by this method. i.e. haematite and cerussite. There are two gravity concentration methods.

## (a) Jigging:

It is removal of the lighter portions of an ore by means of a stream of water or air which rises through a bed of coarse ore particles.

## (b) Tabling:

It is similar removal by passing a mixture of ore and water over an inclined vibrating table.

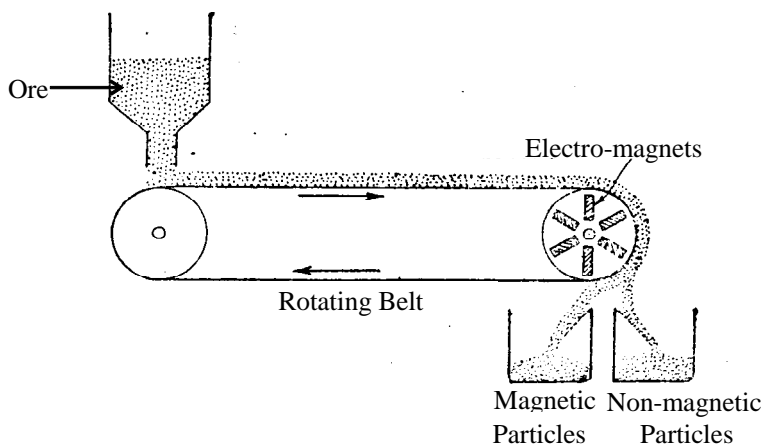


**Gravity Separation or Hydraulic Washing**

## Magnetic Separation

This method of separation is used when either the ore particles or the gangue associated with it possess magnetic properties. For example, chromite  $\text{Fe}(\text{CrO}_2)_2$  being magnetic can be separated from the non-magnetic silicious gangue by magnetic separation. This method is widely used for the separation of two minerals, when one of them happens to be magnetic. The magnetic mineral can be separated from the non-magnetic one by this method.

For example, mixture of  $\text{FeWO}_4$  (magnetic) and cassiterite  $\text{SnO}_2$  (non-magnetic) are separated by this method.



**Magnetic Separation**

Similarly, rutile  $\text{TiO}_2$  (magnetic) can be separated from chlorapatite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$  by magnetic separation.

## Froth Floatation Process

This method is extensively employed for the preliminary treatment of the minerals especially sulphides. The process is based on the difference in wetting characteristics of the gangue and the ore with water and oil. The former surface being preferentially wetted by water and of the latter by oil. The crushed ore along with water

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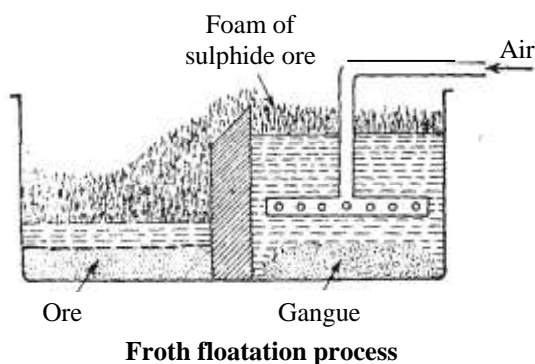
(slurry) is taken in a floatation cell. Various substances (additives) are added depending on the nature of the ore and a current of air is blown under pressure. The air is broken into tiny bubbles which are distributed throughout the volume of the pulp, attaching themselves to those solid particles which have become water repellent after reagent treatment. The bubble–particle aggregates float to the surface of the suspension where a mineral–laden froth forms. The additives added are usually of three types.

**(i) Frothers:** Frothers increase froth stability within desired limit. For example, pine oil, soaps, resins etc.

**(ii) Collectors:** These attach themselves by polar groups to grains of some mineral and form water repelling films on those minerals. Hence, these minerals attach with bubbles and go to froth. Collectors will attach with themselves only to minerals with definite chemical composition and lattice structure. They are high molecular weight organic compounds. The most common among them are xanthates, carboxylic acids and their salts.

**(iii) Activators and Depressants:** Minerals similar in chemical composition, such as sulphides of copper, lead and zinc exhibit an almost equal ability to absorb collectors; for this reason, when present in the same suspension, they will tend to froth together. For the purpose of selective flotation, this tendency may be controlled by supplementary reagents, known as depressors. Depressors are inorganic compounds, which form films on solid particles, thereby preventing the absorption by collectors. The film is produced through a chemical reaction between the depressor and the surface layer of the mineral.

The collector effect, may be enhanced by activators. They are inorganic compounds soluble in water. Added to the suspension, an activator can destroy or modify the depressor film on the solid particles so that they are now able to absorb the collector ions or molecules and become floatable. For example, galena (PbS) is usually associated with zinc sulphide (ZnS), pyrites (FeS<sub>2</sub>) and quartz (SiO<sub>2</sub>). Flotation is carried out by using potassium ethyl xanthate (collector) along with sodium cyanide and zinc vitriol (depressants). They depresses the floatation property of ZnS grains by forming a complex, so mainly PbS passes into the froth when air is blown in. The froth spills over and is collected. After galena has been removed with the froth, the process is repeated by adding CuSO<sub>4</sub> (activator). This break the depressor film on ZnS grains hence, now these grains are available for collector, which are removed with the froth. The acidification of remaining slurry leads to the floatation of pyrites.



## Illustration 1

How does NaCN act as a depressant in preventing ZnS from forming the froth?

### Solution:

NaCN forms a layer of zinc complex,  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  on the surface of ZnS and thus prevents it from the formation of froth.

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## 4. Metallurgical Extraction Methods

These methods are divided into three groups:

(a) Pyrometallurgy (b) Hydrometallurgy (c) Electrolytic Reduction

### 4.1 Pyrometallurgy

It involves the use of elevated temperature and changes in the chemical composition of the entire body of ore. Basic processes of pyrometallurgy are

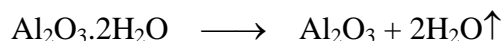
(a) Calcination (b) Roasting (c) Smelting (d) Distillation

#### Calcination

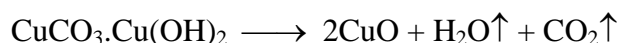
It is a process in which the ore is subjected to the action of heat but is confined to those operations only in which matter is simply expelled or the physical structure altered when heat is applied.



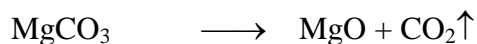
(Lime stone)



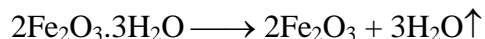
(Bauxite)



(Malachite)



(Magnesite)

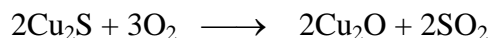
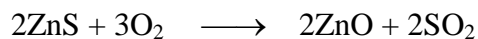
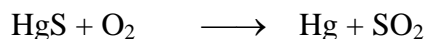
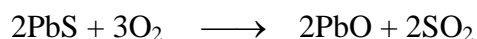
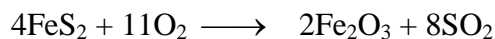


(Limonite)

#### Roasting

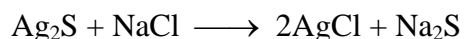
In this process, the ore is heated either alone or in the presence of some substances so that volatile impurities are removed and some chemical changes also take place during this process. It can be of two types.

**(i) Oxidised roasting:** Ores when heated in presence of  $\text{O}_2$  get converted into their oxides and impurities are converted into their volatile form, which do escape.



Roasting or calcination can be carried out in a reverberatory furnace.

**(ii) Chlorinating roasting:** This is done especially in the case of silver ore.



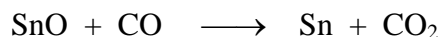
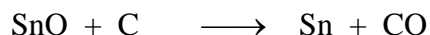
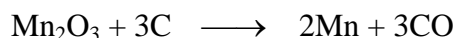
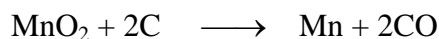
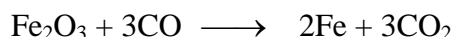
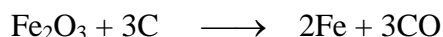
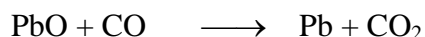
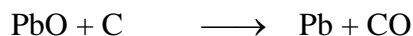
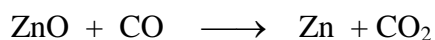
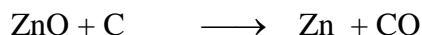
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## Smelting

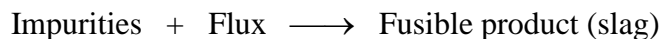
The process of extracting metal from its fused (molten) state is called smelting. The roasted or calcined ore containing metal oxide is mixed with a reducing agent and heated to a high temperature. In this case, a less electropositive metal ore of Pb, Zn, Fe etc. are treated with powerful reducing agent such as C, H<sub>2</sub>, CO etc. Depending upon the nature of the oxide and metal, the extraction of metal can be carried out by the following reducing agents.

### (i) Carbon reduction process

Carbon, the cheapest available reducing agent usually in the form of coke is employed in the extraction of the lead, zinc, iron and tin etc. The oxides of the metals (either naturally occurring or obtained by calcination of the naturally occurring carbonates or roasting of the sulphides) are mixed with coke and heated in a suitable furnace. Carbon or carbon monoxide reduces the oxide to free metal. For example,

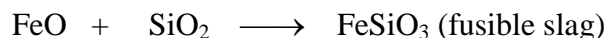


During reduction, additional substance called **flux** is also added to the ore. It combines with impurities to form easily fusible product known as **slag**.

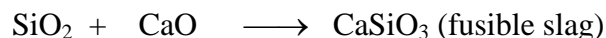


Flux is a substance that is added to the ore during smelting (a) to decrease the melting point (b) to make the ore conducting and (c) to remove all the impurities (basic and acidic).

The nature of the flux depends upon the nature of impurity to be removed. An acidic flux (e.g. sand) is used to remove basic impurities (e.g. metallic oxides like FeO) while basic flux (e.g. CaO) is used to remove acidic impurities (e.g. sand).



Impurity    acidic flux



Impurity    basic flux

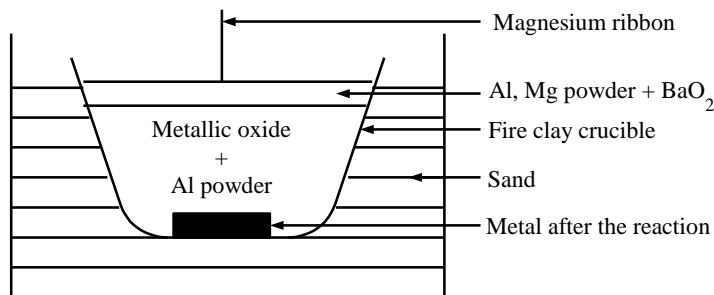
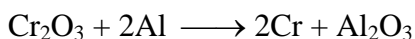
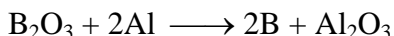
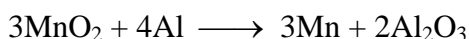
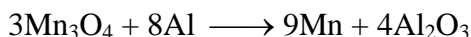
Alumina is a bad conductor of electricity but when cryolite (flux) is added, it becomes a good conductor and the melting point is decreased. Hence, CaF<sub>2</sub>, KF, cryolite etc are neutral flux.

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## (ii) Reduction by another metal (aluminium)

If the temperature needed for carbon to reduce an oxide is too high for economic or practical purposes, the reduction may be effected by another highly electropositive metal such as aluminium, which liberates a large amount of energy ( $1675 \text{ kJ mol}^{-1}$ ) on oxidation to  $\text{Al}_2\text{O}_3$ . This process of reduction of a metal oxide to metal with the help of aluminium powder is called aluminothermy or Goldschmidt Aluminothermic Process or Thermite process.

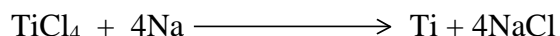
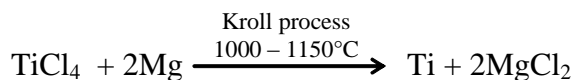
This process is employed in the case of those metals, which have very high melting points and are to be extracted from their oxides. A mixture of concentrated oxide ore and aluminium powder, commonly called as thermite is taken in a steel crucible placed in a bed of sand. The reaction is initiated by the use of an ignition mixture containing magnesium powder and barium peroxide. During the reaction, aluminium gets oxidised to  $\text{Al}_2\text{O}_3$  while metal oxides releases metals.



### Goldschmidt Aluminothermic Process

Sr and Ba are obtained by the reduction of their oxides by aluminium in vacuum.

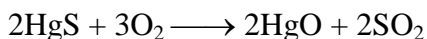
Magnesium is used in a similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce metal halides. Titanium (for supersonic aircrafts) and zirconium (used in atomic reactors) are obtained by the reduction of their tetrachlorides with metallic sodium or magnesium.



## (iii) Self-reduction process

The cations of the less electropositive metals like Pb, Hg, Sb and Cu may be reduced without the use of any additional reducing agent. Elevated temperatures and anion or anions associated with the metal may bring about this change.

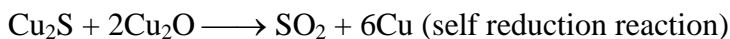
For example, in the extraction of mercury, the sulphide ore (cinnabar) is heated in a current of air when the following reactions take place.



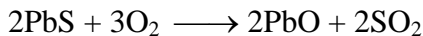


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Similarly, in the extraction of copper, the sulphide and the oxide interact at an elevated temperature to give the metal.

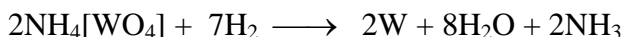
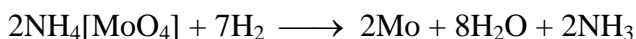
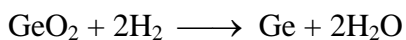
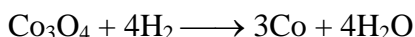


Similar reactions take place in the self-reduction process for the extraction of lead.



### (iv) Reduction of oxides with hydrogen

Certain metallic oxides can be reduced using molecular hydrogen. Because of inflammable nature of hydrogen, it is used in very few cases. Molybdenum and tungsten are obtained by reducing their oxides by hydrogen at elevated temperatures.

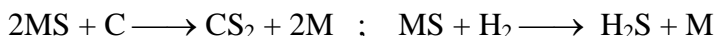


This method is not widely used because many metals react with hydrogen at elevated temperature, forming hydrides. There is also a risk of explosion from hydrogen and oxygen present in the air.

### Illustration 2

Why is it advantageous to roast a sulphide ore to the oxide before reduction?

#### Solution:



The free energies of formation of most sulphides are greater than those for  $\text{CS}_2$  and  $\text{H}_2\text{S}$ . So, the net reactions have unfavorable free energy of formations. Thus, neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Aluminium cannot be used, as reaction with metal sulphide would produce aluminium sulphide, which is not so exothermic. So, sulphide ores are preferentially converted to oxide ores as any reduction method (reduction by C,  $\text{H}_2$ , Al etc.) could then be conveniently used.

### Distillation

It is a process by which the metal or its chemical compounds are evaporated to liberate them from the non-volatile components of the charge. The vapours of the metal or its compounds are then condensed in a more or less pure state.

## 4.2 Hydrometallurgy

It is based on dissolving the metal sought in aqueous solutions of acids or alkalis and subsequent precipitation. Basic processes of hydrometallurgy are

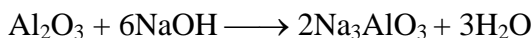
(a) Leaching (b) Thickening (c) Precipitation

### Leaching

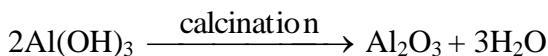
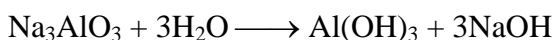
This is a chemical method of concentration. Here the powdered ore is treated with certain reagents, which dissolves the ore leaving behind impurities. The impurities left undissolved are removed by filtration. Leaching method is used for concentrating ores of aluminium, silver, gold etc. For example, bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ), is

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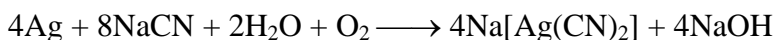
concentrated by this method. Crude bauxite contains ferric oxide, titanium oxide and silica. These impurities are removed by making use of the amphoteric nature of alumina. Finely powdered bauxite is treated with an aqueous solution of caustic soda at 420–440 K under pressure for several hours. Alumina present in bauxite dissolves forming soluble sodium aluminate.



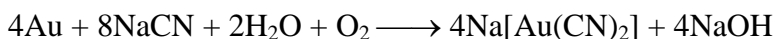
The impurities remain unaffected and separate as insoluble red mud, which is filtered off. The filtrate is diluted and a little freshly precipitated aluminium hydroxide is added which causes the precipitation of aluminium hydroxide. This is filtered and calcinated to get highly pure alumina.



Leaching is also used to concentrate silver and gold ores and is known as Mac Arthur Forrest cyanide process.

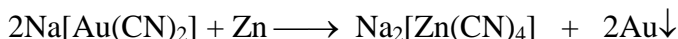
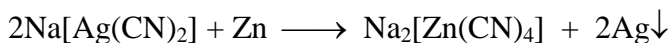


(Sodium argentocyanide)



(Sodium aurocyanide)

Now, Ag and Au can be recovered easily from the solution by the addition of electropositive metal like zinc.



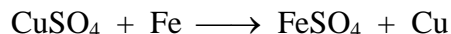
Soluble complexes

### Thickening

Prior to precipitation, it is sometimes advantageous to concentrate the solution. This is especially true of lean materials, the leached solution of which are usually diluted or contain large amount of impurities. This concentration is called thickening. It is accomplished by means of ion–exchange method.

### Precipitation

The metal sought or its compounds obtained by leaching are precipitated from the solution after it has been separated from the undissolved residue by means of filtering or settling. In elemental form, a metal can be precipitated from a solution either electrolytically, as in case of copper, zinc or nickel or by cementation according to reaction.



### 4.3 Electrolytic Reduction

The strongest possible reducing agent is an electron. Any ionic material may be electrolysed and reduction occurs at the cathode. This is excellent method and gives very pure products but electricity is quite expensive. Electrolysis may be performed in aqueous solution provided that the products do not react with water.

This process is mainly used in the extraction of alkali and alkaline earth metals. In the case of highly electropositive metals, isolation by chemical reducing agents is extremely difficult. In such cases, the metal is obtained by electrolysis of fused salts. Under such conditions, the ions readily move to the oppositely charged

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electrodes and are distinguished and discharged over there. Some other salts may have to be added to lower the melting point of the compound taken.

## 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. (The reaction has many technical difficulties (i) HF is corrosive (ii) hydrogen produced at the cathode must be kept separate from the fluorine produced at the anode otherwise explosion may occur (iii) water must be rigorously excluded (iv) fluorine produced attacks the anode and the reaction vessel).

## In fused melts:

Elements that react with water are often extracted from fused melts of their ionic salts. These melts are frequently corrosive and involve large fuel bills to maintain the high temperature required. Aluminium is obtained by 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 up to two-thirds by weight of  $\text{CaCl}_2$  is added as an impurity to lower the melting point from  $803^\circ\text{C}$  to  $505^\circ\text{C}$ .

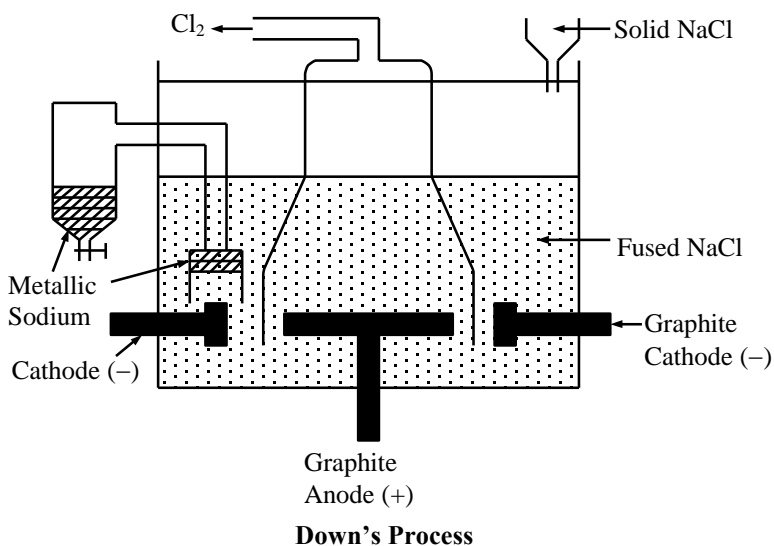
An example of this is the manufacture of sodium by electrolysis of a fused mixture of sodium and calcium chlorides (Down's process). The cell and electrodes used should not be effected by the electrolyte or the products. Hence a steel cell, a graphite anode and an iron cathode are employed. The various reactions that take place are,

On fusion,  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$  (ions become mobile)

On electrolysis, (i) At the cathode (negative electrode):  $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$  (reduction)

(ii) At the anode (positive electrode):  $\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$  (oxidation) ;  $\text{Cl} + \text{Cl} \longrightarrow \text{Cl}_2$

The products obtained react readily, hence a suitable arrangement has to be made to keep them separate.



## 5. Thermodynamics of Metallurgy

The method employed for extracting a metal from its ores depends on the nature of the metal and that of the ore and may be related to the position of the metal in the electrochemical series. In general, metals with  $E^\circ < -1.5$  volt yield compounds which are very difficult to reduce and electricity is usually used for the isolation of such metals. On the other hand, noble metals with  $E^\circ > +0.5$  volt form easily reducible compounds. A metal higher

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up in the electrochemical series should be more difficult to reduce to metallic form. As we move down, the reduction becomes more and more easy.

Standard electrode potential of a metal provides some idea regarding the selection of an appropriate method for extracting the metal from its compounds. However, the free energy changes ( $\Delta G$ ) occurring during the reduction processes are of more importance and help in deciding the suitable method.

In order that the reduction of an oxide, halide or sulphide ore by an element may take place spontaneously at a given temperature and pressure, it is essential that there is a decrease in the free energy of the system (negative  $\Delta G$ ). As a matter of fact, the more the negative value of  $\Delta G$ , the higher is the reducing power of an element.

The free energy change ( $\Delta G$ ) is related to the heat change ( $\Delta H$ ) as well as to the product of temperature ( $T$ ) and the entropy change by an expression

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

When all the reacting substances are at unit activity,  $\Delta G = \Delta G^\circ$  (standard free energy change).

For a reaction such as the formation of an oxide,



$\Delta G$  becomes smaller with the increase in temperature. This is because the gaseous reactant oxygen is consumed in the reaction leading to the decrease in randomness or entropy ( $S$ ) of the system and consequently  $\Delta S$  becomes negative. With further increase in temperature,  $T\Delta S$  acquires more negative value. Since the term  $T\Delta S$  is subtracted from  $\Delta H$ ,  $\Delta G$  will become increasingly less negative with increase in temperature.

## 6. Factors Influencing the Choice of Extraction Process

The type of process used commercially for any particular element depends on a number of factors.

- (i) Is the element unreactive enough to exist in the free state?
- (ii) Are any of its compounds unstable to heat?
- (iii) Does the element exist as an ionic compound, and is the element stable in water? If both are true, is there a cheap element above it in the electrochemical series, which can be sacrificed to displace it from solution?
- (iv) Does the element occur as sulphide ores, which can be roasted or oxide ores, which can be reduced using carbon, is the cheapest whilst the use of Mg, Al and Na as reducing agents is more expensive.
- (v) If all other methods fail, electrolysis usually works for ionic materials, but is expensive. If the element is stable in water, electrolysis of aqueous solutions is cheaper than using fused melts.

## 7. Refining or Purification of Metals

Metals obtained by reduction processes still contain some objectionable impurities and hence have to be refined. Refining techniques vary widely from metal to metal and also depend on the use to which a metal has to be put. Sometimes during refining some substances may have to be added to impart some desirable characteristics to the metal. In some cases a metal is refined to recover valuable by-products present as impurities. Some of the refining processes used are defined below.

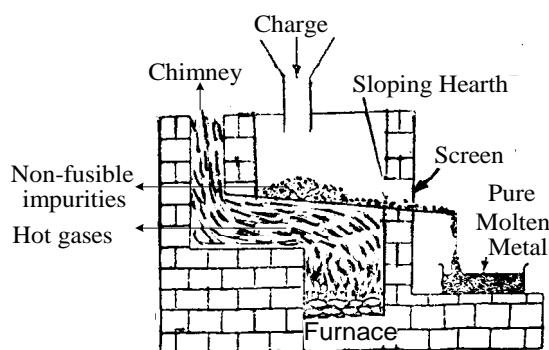
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## 7.1 By Poling

This method is employed when the metal contains the impurities present in the form of its oxide. To reduce the impurity level, air is blown through molten metal to which a suitable flux may be added. Impurities are oxidized and escape as gases ( $\text{CO}_2$ ) or pass into slag. Finally the surface of molten metal is covered with low sulphur coke (to prevent oxidation of the metal) and green logs of wood are introduced into the molten metal. Hydrocarbon gases reduce any oxide of the metal that might have been formed. This method is used for the purification of Cu and Sn.

## 7.2 By Liquation

Readily fusible metals like Sn, Pb and Bi are refined by this method. Impure metal in the form of ingots blocks is placed in the upper part of a sloping hearth (usually of a reverberatory furnace) maintained at a temperature slightly above the melting point of the metal.



Liquation Process

The impurities remain behind as dross while the pure metal melts and flows down into a well at the bottom of the incline.

## 7.3 By Cupellation

This is a method employed to purify silver containing lead as an impurity. The impure silver is heated in a shallow vessel made of bone-ash under a blast of air. The lead is easily oxidised to powdery lead monoxide. Most of it is carried away by the blast of air. The rest melts and is absorbed by the bone ash cupel. Pure silver is left behind. Silver itself is not oxidised under these conditions.

## 7.4 By Distillation

Some metals have very low melting point and soon vaporise on heating while the associated impurities remain in the solid state. Zinc, mercury and arsenic are purified by this method. Vacuum distillation gives very pure product and is used in the refining of the metals of IA and IIA.

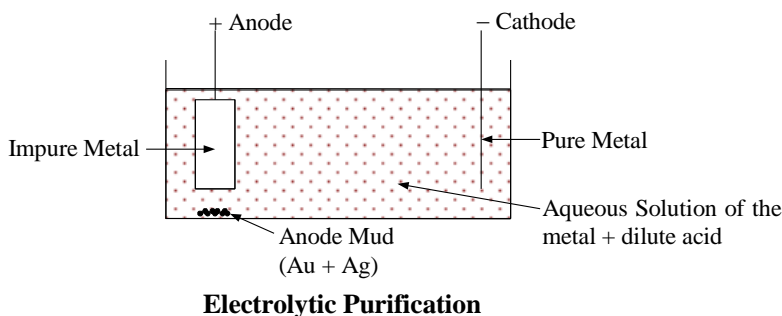
## 7.5 By Fractional Distillation

This process is applied for the separation of cadmium from zinc. In the metallurgy of zinc, the metal is invariably associated with cadmium. The impure zinc is mixed with powdered coke and heated when the first portion of the condensate contain cadmium while zinc is obtained in the subsequent portions.

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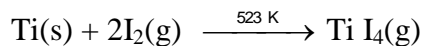
## 7.6 By Electrolytic Refining

This is a very convenient method for refining many impure metals. Most of the metals such as copper, silver, gold, zinc and chromium are refined electrolytically. The impure metal is made the anode and a thin sheet of the pure metal as cathode. A solution of a salt of the metal serves as the electrolyte. On passing an electric current through the electrolyte, the metal dissolves in the electrolyte by oxidation of the anode and pure metal is deposited at the cathode. The impurities present in the anode either dissolve in the electrolyte or collect below the anode as anode mud. In the electrolytic refining of copper, impurities of iron and zinc are dissolved in the electrolyte and while gold, platinum and silver are left behind as anode mud.

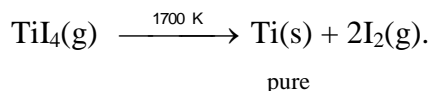


## 7.7 Van-Arkel Method

This is used for getting ultra pure metals. The principle involved is to convert the metal to a volatile unstable compound and to subsequently decompose it to give the pure metal. The impurities present should be such as not to be affected. Metals like titanium, zirconium etc. are purified by using this method.

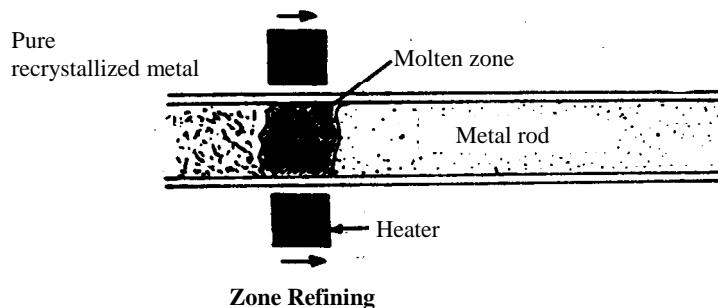


Impure



## 7.8 Zone-Refining

Metals of very high purity can be obtained by this method by removing an impurity, which shows difference in solubility of the liquid and solid states of the metal. A circular heater is fitted around a rod of impure metal and is slowly moved down the rod. At the heated zone, the rod melts and as the heater passes on, pure metal crystallizes while impurities pass into the adjacent molten part. In this way, the impurities are swept over one end of the rod, which is finally discarded. The heater may have to be moved from one end to the other more than once. Ge, Si and Ga used as semiconductors are refined in this manner; gallium–arsenide and indium–antimonide are also zone refined.



## 7.9 Chromatography (Ion Exchange Method)

Chromatography is based on the differential adsorption of the various components in a mixture on a suitable adsorbent. In its various forms like column chromatography, TLC (Thin Layer Chromatography), GLC (Gas Liquid Chromatography), Ion-exchange chromatography and Paper chromatography, it is widely used for the separation of mixtures and concentration, identification and refining of materials.

## 8. Furnaces Used in Metallurgy

Some of the principal furnaces used are the following:

### 8.1 Kilns

These are the structures of enclosures in which the materials are mixed with proper fuel, free access of air is permitted but no fusion takes place. The kilns are sometimes heated by gas or by the waste heat from other furnaces.

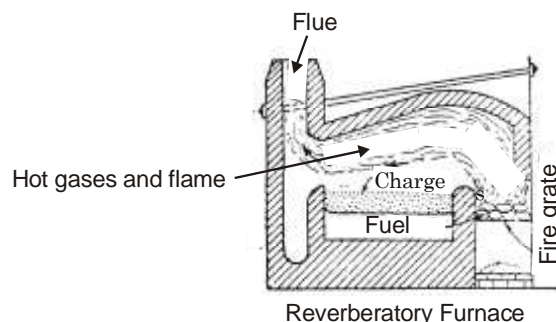
### 8.2 Blast Furnaces

These are tall structures with gate at the bottom and openings at the top. An air blast is supplied to the furnace by means of blow fans or blowing engines through nozzles provided at the bottom; the nozzles are called tuyers. The materials to be treated are charged into the furnace mixed with the fuel and as the substances melt, they run down to the bottom and accumulate in the space below the tuyers known as hearth. When sufficient material has accumulated into the space a hole is tapped into the furnace and the molten matter is allowed to flow out in a separate receiver. Such blast furnaces are obviously utilised for fusions of reducing character, in which the carbonaceous matter of the fuel acts as the reducing agent. In them, the combustion takes place near the region at which the air is blown in and the ascending stream of gases is cooled by the material in the upper part of the furnace. The extent of cooling depends on the rate of ascent and the height of the column.

### 8.3 Reverberatory Furnace

These are the furnaces in which the fuel is burnt in a separate part of the structure, the flame and hot gases only coming into contact with the material treated. The chamber in these furnaces is horizontal and is divided into two equal parts by a bridge like partition. The smaller part is the fireplace, closed with fire-bars below.

The larger portion is the laboratory of the furnace, the bottom of which is known as the bed or hearth. The materials are placed on this bed for treatment. Opposite to the fireplace at the other end, is the fine bridge which communicates with stack or chimney. The roof of the furnace gradually takes a bend towards the flue end and the whole concave bend deflects or reverberates the flame and hot gases from the fire downward, the roof comprising the concave bend becomes heated and radiates heat on the bed. As the fuel does not come directly in contact with the material, the reverberatory furnace can be utilised both for reduction and oxidation processes. If reduction be desired the material is mixed with a reducing agent.





## 8.4 Muffle Furnaces

It is sometimes desired for certain reasons to exclude the products of combustion as well as the fuel and this is accomplished in muffle furnaces. The muffle is a chamber surrounded by the fire or by flues through which the products of combustion and hot gases from the fire pass. These furnaces are used for annealing and gold and silver assaying.

## 8.5 Regenerative Furnaces

The heat carried away to the flues by the escaping gases is again utilised in these furnaces. A flowing column of air is heated by the hot flue gases, the air is then brought back to the fire and returned to the furnace. This means an economy of fuel. Most of the furnaces are fitted up with regenerative systems.

## 8.6 Electric Furnaces

Such furnaces are largely used where cheap power is available and very high temperatures are required and also for electrolytic reductions. The furnaces may be classified as (a) Induction furnaces, in which the charge lying on the furnace bed or in a crucible constitutes the secondary coil of an induction unit, and the induced current produced by making and breaking the primary circuit, heat up the material, (b) Resistance furnaces, in which the heat generated by resistance in the circuit is utilised. In some of the furnaces, the body of the furnace itself is made of a resistance material. Small furnaces may be prepared by heat is generated by arcs and thereby, a temperature of over 3000°C current and the arc is struck between them and the charge.

Besides these, there are many types of furnaces such as Bessemer converter, Heroult's furnace etc. which are used in metallurgy.

## 9. Copper & Its Metallurgy

### Extraction

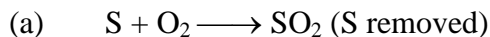
The chief and important ore of copper from which the metal is mostly isolated is copper pyrites ( $\text{CuFeS}_2$ ). It involves the following steps:

#### Concentration

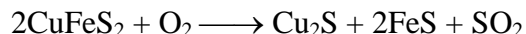
Froth floatation process is used for concentrating the ore. The powdered ore is suspended in water and after adding little pine oil is stirred by means of air. The sulphide ore particles come to the surface & gangue remains at the bottom is rejected.

#### Roasting

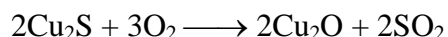
The concentrated ore is heated strongly by the current of air on the hearth of reverberatory furnace whereby following reactions takes place.



(c) The copper pyrite is partially converted into sulphide.



(d) The sulphides are further partially converted into oxides.





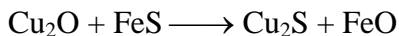
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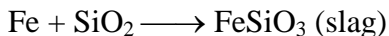


## Smelting

The roasted ore ( $\text{Cu}_2\text{S} + \text{FeS} + \text{Cu}_2\text{O} + \text{FeO}$ ) mixed with coke and sand is heated in water jacketed blast furnace.



This ferrous oxide combines with silica to form ferrous silicate as slag.



The slag being lighter than molten mixture of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  (copper matte) floats & is removed. Copper matte contains 50% Cu.

## Bessemerization

The molten copper matte is introduced into a small pear shaped furnace of steel plates called “Bessemer’s converter”.



This copper obtained is known as blistered copper. It contains about 2% impurities mainly of As, Sn, Pb, Ag, Au, Ni, Zn etc.

## Refining

It is done by two methods:

### Refining by Poling

By this method, we can obtain 99.5% pure copper.

### Electrolytic Refining

Cathode	:	Pure copper
Anode	:	Impure copper
Electrolyte	:	85% $\text{CuSO}_4$ containing 5% dilute $\text{H}_2\text{SO}_4$ taken in a lead lined tank.

This method gives 99.9% pure copper.

Copper Pyrites ( $\text{CuFeS}_2$ )

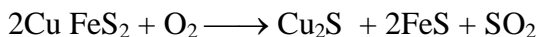
↓ Crushed and sieved

Concentration by froth floatation

i.e., powdered ore + water + pine oil + air  $\longrightarrow$  sulphide ore in the froth.

↓

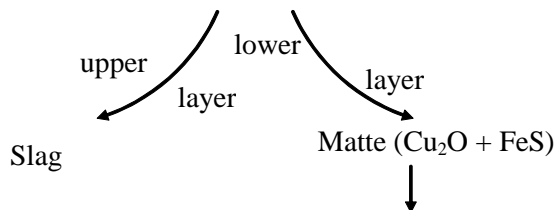
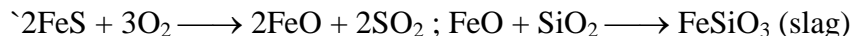
Roasting in reverberatory furnace in pressure of air



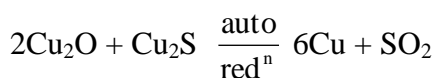
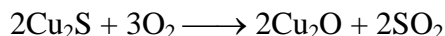
↓ sand + coke

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Smelting in blast furnace in pressure of air



Bessemerization in Bessemer converter in pressure of air



Blister copper (98% Cu + 2% impurities)

Electrolytic refining

- Anode : impure copper plates
- Cathode : Pure copper plates
- Electrolyte :  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$

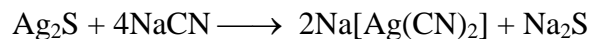
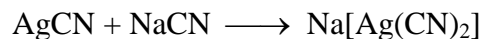
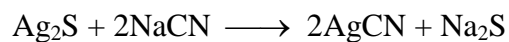
Pure copper at cathode (99.9% pure).

## 10. Silver & Its Metallurgy

**Occurrence:** It occurs in free state. The chief and important ore of silver is silver glance ( $\text{Ag}_2\text{S}$ ), which is present as such or is associated with galena,  $\text{PbS}$ .

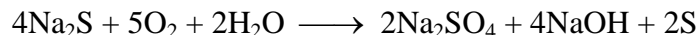
### 10.1 Cyanide Process (Mac Arthur Forrest) Process

The finally powdered ore after being concentrated by froth floatation process is treated with dilute (0.7%)  $\text{NaCN}$  solution and a current of air is blown into it. The silver present in the ore dissolves forming a complex soluble salt sodium argentocyanide.

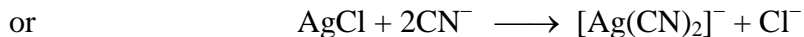
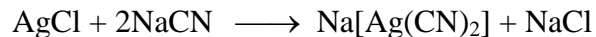


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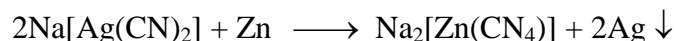
The reaction is reversible and in order to prevent backward reaction it is essential to remove sodium sulphide from the sphere of action. The oxygen of the air converts sodium sulphide into sodium sulphate and free sulphur and thus makes the above reaction irreversible.



In case the ore is silver chloride then, too, it goes into solution forming sodium argentocyanide.



The solution of sodium argentocyanide, obtained as above, is treated with finely powdered zinc. Zinc being more electropositive than silver displaces it from the solution. A black precipitate of silver is thus obtained.



The precipitated silver is mixed with potassium nitrate and fused when the impurities are oxidised and removed as a scum from the surface of molten metal. On cooling a compact shining mass of silver is formed.

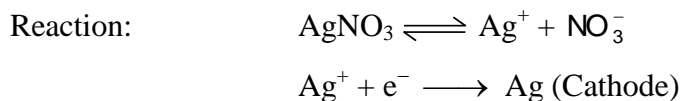
This is the best method of extracting silver from its ore especially when the % of silver is low.

## 10.2 Refining of Silver

Silver so obtained is purified by electrolytic process. It consists of:

Cathode	Pure Ag
Anode	Impure Ag
Electrolyte	$\text{AgNO}_3$ solution containing 1% $\text{HNO}_3$

On passing electric current pure silver is deposited on cathode while the same amount dissolves out from anode. The more electro positive metals like copper and zinc remain in solution while less electro positive gold comes down as anode mud.



## 11. Gold & Its Metallurgy

### 11.1 Occurrence

Gold occurs both in free and combined state.

(i) **Native state:** It is generally found in free state because it is a noble metal. The two important sources are

(a) **Quartz veins:** In this state, the fine particles of gold along with silver and platinum remain embedded.

(b) **Alluvial sands:** This is present in those rivers, which passes over auriferous rocks.

(ii) **Combined state:** Its compounds in nature are few. Bismuth surite  $\text{AuBi}$ , Calaverite  $\text{AuTe}_2$ .

### 11.2 Extraction of Gold

Gold is extracted from quartz veins and alluvial sands by the following methods:

(i) **Amalgamation process**

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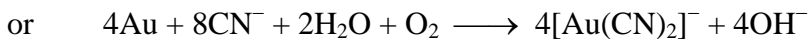
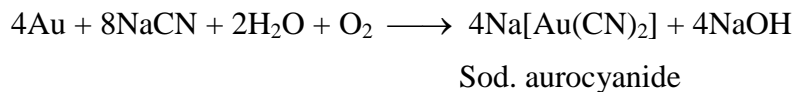
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## (ii) Cyanide process

## (iii) Chlorination process

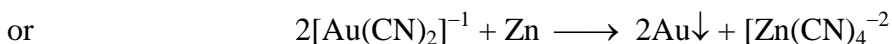
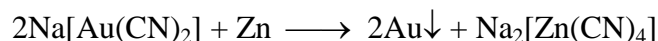
### Cyanide process (Mac Arthur Forrests)

This is very good process for the removal of traces of gold from tailings of amalgamation process or from even poorer ores. It is based on the fact that gold dissolves in dilute solution (0.3%) of sodium cyanide in presence of atmosphere oxygen with the formation of complex cyanide.



### Alternative method:

The finely powdered ore from the stamp mill or tailings of amalgamation process is taken in large wooden vats provided with perforated false bottom covered with coconut matting. It is then treated with 0.3% NaCN solution in presence of excess of air for about 24 hours. The solution of sodium aurocyanide so obtained is treated with metal zinc when gold being less electropositive precipitated out.



The precipitated gold is treated with dil.  $\text{H}_2\text{SO}_4$  to remove excess of zinc.

## 12. Magnesium and Its Metallurgy

The compound known as Epsom salt (Magnesium sulphate) was isolated from spring water in Epsom (England) in 1795. Davy isolated the metal in the impure state in 1809 electrolytically and called it "Magnium", which was later changed to Magnesium.

Magnesium is extracted by

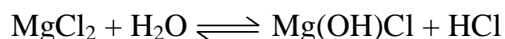
1. Modern Electrolytic method
2. Electrolysis of  $\text{MgO}$
3. Reduction of  $\text{MgO}$
4. Sea water

### 12.1 Modern Electrolytic Method

#### From fused $\text{MgCl}_2$

Magnesium is obtained by the electrolysis of fused  $\text{MgCl}_2$  but the process is met with the following difficulties:

- (i) Fusion temperature of  $\text{MgCl}_2$  is quite high.
- (ii) It is not good conductor of electricity.
- (iii)  $\text{MgCl}_2$  may be hydrolysed by water present in carnallite to form magnesium hydroxy chloride.



- (iv) On electrolysis of  $\text{MgCl}_2$ , Mg metal liberated at cathode may come in contact with chlorine which is liberated at anode.

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(v)  $O_2$  and  $N_2$  of the air present in the vessel may react with molten metal.

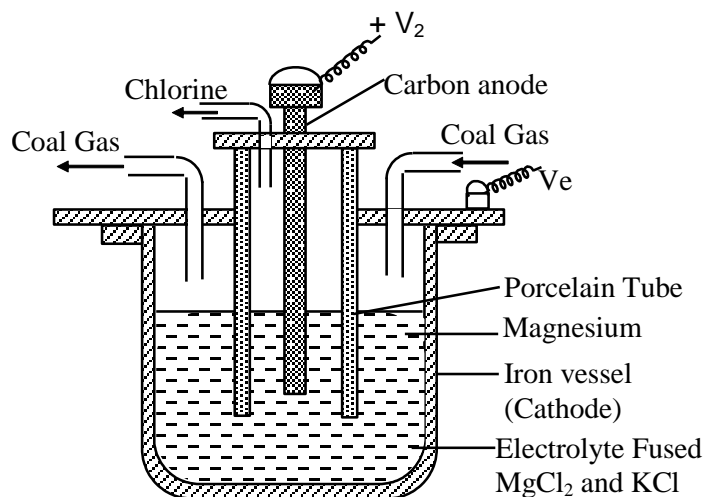
To overcome the above difficulties:

- (a) The electrolyte used is fused  $MgCl_2$  to which some  $NaCl$  has also been added. The later reduces the melting point, increases the conductivity of the electrolyte and prevents the hydrolysis of magnesium chloride.
- (b) The air of the apparatus is displaced by an inert gas such as coal gas or hydrogen.
- (c) The electrolysis is carried out in iron cell which acts as cathode. A graphite anode is surrounded by a porcelain hood to escape chlorine.

On electrolysis magnesium is liberated and being lighter floats on the surface of the electrolyte and is drawn off. It is about 92.0% pure.

### From fused Magnesium Chloride by Electrolysis

Magnesium is also obtained by the electrolysis of magnesium chloride dissolved in used mixture of magnesium, potassium and sodium chlorides at  $950^\circ C$ , Magnesium is liberated at cathode while chlorine is evolved at anode.



## 13. Aluminium and Its Metallurgy

Aluminium is the most abundant metal in the earth's crust. Aluminium does not occur free in nature, but its compounds are numerous and widely distributed.

The chief and important ore from which aluminium is exclusively and profitably obtained is Bauxite,  $Al_2O_3 \cdot 2H_2O$ . The extraction of the metal from bauxite involves the three main steps.

(A) Purification of Bauxite, (B) Electrolytic reduction of Alumina, ( $Al_2O_3$ ) (C) Purification of Al.

### 13.1 Purification of Bauxite

Bauxite is either white or brown in colour depending upon the presence of too much  $SiO_2$ ;  $TiO_2$  or  $Fe_2O_3$  respectively. the purification is carried out as below

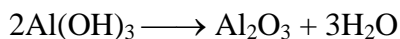
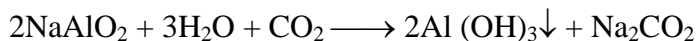
#### Hall's Dry Process

Bauxite is fused with sodium carbonate. Sodium meta aluminate,  $NaAlO_2$ , is produced which is soluble in water. It is extracted with water. The impurities present viz. ferric oxide and silica, are left behind.

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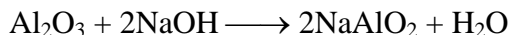


The water extract is heated to  $50^\circ - 60^\circ\text{C}$  and a current of carbon dioxide is passed through it. Aluminium hydroxide is ignited to obtain pure alumina.



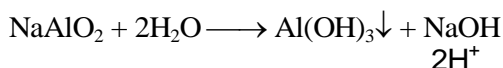
### Baeyer's Process

(For ores containing much of  $\text{Fe}_2\text{O}_3$ ): The calcined bauxite is digested with strong  $\text{NaOH}$  solution at  $150^\circ$  under pressure when alumina ( $\text{Al}_2\text{O}_3$ ) dissolves out leaving behind oxides of iron, titanium as residue.



Sod. aluminate

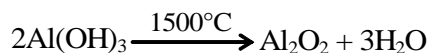
The mass is filtered and the filtrate is stirred with freshly precipitated  $\text{Al}(\text{OH})_3$ . Sodium meta-aluminate in the filtrate is hydrolysed and is changed into aluminium hydroxide as precipitated.



$2\text{H}^+$



The precipitate is filtered off, washed, dried and heated to get pure alumina (rotary furnace).

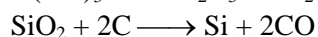
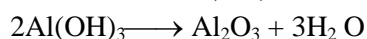
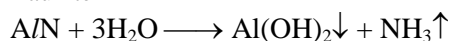


### Serpeck's Process (when ores contains lot of silica, $\text{SiO}_2$ )

The ore is heated with carbon at  $1800^\circ\text{C}$  and nitrogen is passed over it. Aluminium nitride is formed which on hydrolysis with water yield  $\text{Al}(\text{OH})_3$ . This is separated and calcined to get alumina.



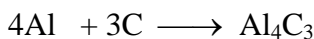
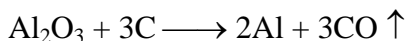
Bauxite



Silica is present as impurity is reduced by carbon to silicon, which evaporates at the high temperature.

(b) Electrolytic reduction of pure  $\text{Al}_2\text{O}_3$  (Hall and Heroult's process, 1886)

Aluminium metal has great affinity for oxygen and thus the reduction of its oxide by carbon is not possible under ordinary conditions. It does take place at very high temperature and Al metal formed reacts with carbon forming aluminium carbide ( $\text{Al}_4\text{C}_3$ ).



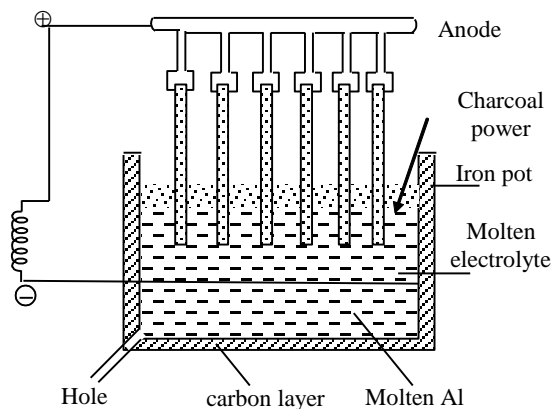
The reduction is however, possible electrolytically, but is encountered with the following difficulties.

(a) Pure  $\text{Al}_2\text{O}_3$  is a bad conductor of electricity and has high melting point i.e., above  $2000^\circ\text{C}$ .

If electrolysis of fused alumina is carried out, metal aluminium formed will vaporise off as its boiling point is about  $1800^\circ\text{C}$ .

## 13.2 Principle of Extraction

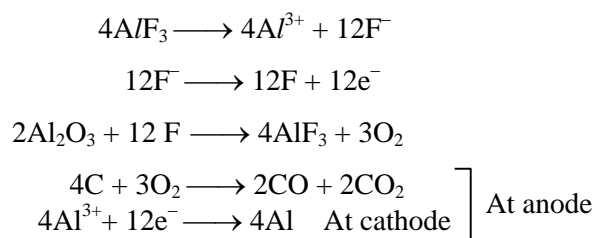
Alumina is mixed with cryolite ( $\text{Na}_3\text{AlF}_6$ ), fluorspar ( $\text{CaF}_2$ ) in the ratio 20 : 60 whereby, it not only becomes good conductor but also fuses at about  $900^\circ\text{C}$  which is much below the b.p. of aluminium.



The electrolysis of the fused mass is carried out in an iron box, which is lined with gas carbon. The lining serves as the cathode, the anode consists of carbon rods dipped in the fused mass. The fused electrolyte is kept covered with a layer of powdered coke to prevent any action of air. The voltage employed in the electrolysis is 5.3 volts. The current passed (about 50,000 amperes) serves two purposes: (i) heating and (ii) electrolysis. Thus the fused mass is automatically kept at  $900^\circ\text{C}$  during electrolysis.

Aluminium is obtained at the cathode and being heavier than the electrolyte sinks to the bottom and is tapped off periodically from the tap hole. Oxygen liberated at the anode attacks carbon rods and forms CO and  $\text{CO}_2$ . During electrolysis the concentration of the electrolyte goes on falling thereby increasing the resistance of the cell which is indicated by the glowing of a lamp placed parallel. Much of the alumina is then added and the process is made continuous.

The probable reactions may be given as

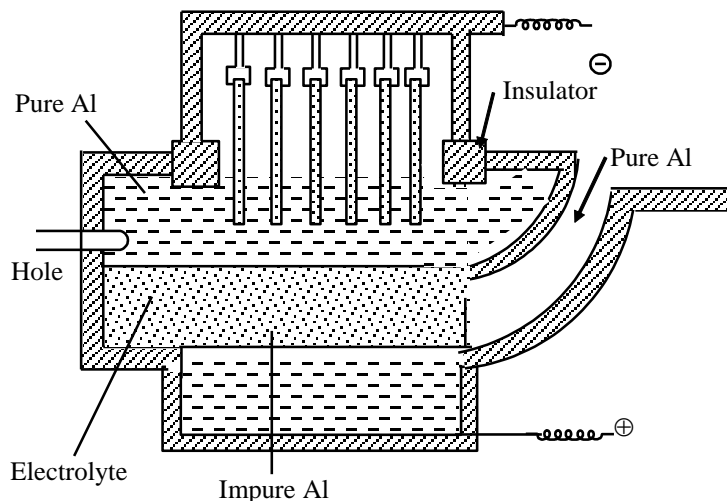


## 13.3 Purification

Aluminium as produced by the electrolysis of  $\text{Al}_2\text{O}_3$  is 90% pure. It can be refined further up to 99.9% purity by Hoopes' process.

The electrolytic cell consists of an iron tank lined with carbon. It is filled with three liquids differing in specific gravity. The upper layer is of pure fused aluminium and serves as cathode.

The bottom layer is that of impure metal in the fused state and serves as anode. The central layer is that of molten mixture of the fluorides of Al, Ba and Na and serves as an electrolyte.



On passing electric current, pure aluminium goes to the top layer from the central layer and an equivalent amount of the metal from the bottom layer passes into the central layer. There is thus a gradual transference of aluminium from bottom layer to the top and the impurities are left behind. Crude aluminium is added from time to time.

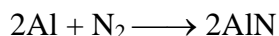
## 13.4 Properties of Aluminium

### Physical Properties

- (i) It is a bluish white metal with a brilliant lustre.
- (ii) It is a light metal and its density is 2.7.
- (iii) Its melting point and boiling point are 658.7°C and 1800°C respectively.
- (iv) It is good conductor of heat and electricity.
- (v) It forms alloys with other metals.

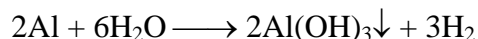
### Chemical Properties

- (i) Action of air: It is not affected by dry air but in moist air a film of oxide is formed on the surface. It burns in oxygen producing oxide.

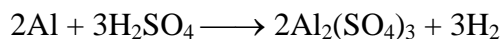
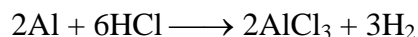


- (ii) Action of water: Pure aluminium is not affected by pure water but impure metal is corroded by water containing some impurities.

It decomposes by boiling water evolving hydrogen.



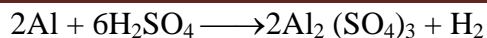
- (iii) Action of acids: (a) Dilute HCl and H<sub>2</sub>SO<sub>4</sub> produce hydrogen with Al.



(b) Hot and concentrated H<sub>2</sub>SO<sub>4</sub> produces sulphur dioxide.

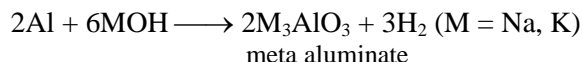
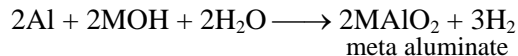


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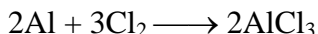


(c) Concentrated  $\text{HNO}_3$  does not react with Al as Al forms a self protecting coating of  $\text{Al}_2\text{O}_3$  which renders  $\text{HNO}_3$  unreactive towards Al. This is called passivity of Al.

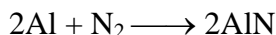
(iv) Action of alkalis: When Al-powder is boiled with NaOH solution,  $\text{H}_2$  is liberated and soluble aluminates are formed.



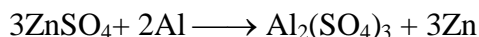
(v) Action of halogens: When halogens are passed over heated aluminium halides are formed.



(vi) Action of nitrogen: Aluminium when heated with nitrogen gas gives aluminium nitride.



(vii) Displacement of other metals: Aluminium displaces copper, zinc and lead from the solutions of their salts because these metals are less electropositive than Al. (see electrochemical series).



### 13.5 Uses of Aluminium

- (i) Aluminium, being very light, is used in household utensils, aeroplane parts, precision and surgical instruments etc.
- (ii) Since it is unattacked by nitric acid, is used in chemical plants and also for transporting nitric acid.
- (iii) Aluminium foil is used for packing chocolates, cigarettes etc.
- (iv) Alums are used as mordants in dyeing and points.
- (v) Mixed with oil, it is used in steam piped and other metal objects.
- (vi) It is used as a reducing agent for the production of certain metals such as chromium, iron, manganese etc.
- (vii) Alumina is used for making refractory bricks and ultramarine.

### 13.6 Aluminium Alloys

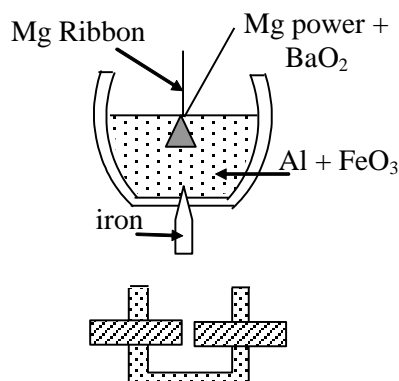
Aluminium forms a number of useful alloys, which are given as follows;

Alloy	Approximate composition	Uses
(1) Aluminium bronze	Al 10%, Cu 90%	For hard, non-corrodible vessels
(2) Duralumin	Al 95%, Cu 3% Mn 1% Mg 1%	Aeroplanes and automobile parts
(3) Magnalium	Al 90%, Mg 10%	Balance beams
(4) Y-alloy	Al 92.5%, Cu 4%, Ni 2%, Mg 1.5%	Aeroplanes, non-corrodible vessels.

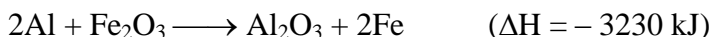
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## 13.7 Goldschmidts' Aluminothermic Process

The evolution of enormous quantities of heat in the oxidation of aluminium is used in thermite welding of metals. This process is also known as Goldschmidts aluminothermic process.



A mixture containing 3 parts of ferric oxide and one part of aluminium powder is placed in a crucible lined with magnesite and having a plug hole (see figure). This is covered with a layer of mixture of magnesium powder and barium peroxide, with a magnesium ribbon inserted into it to act as a fuse. The broken ends of a rail or a girder etc. are brought nearer and thoroughly cleaned and surrounded by a fire-clay mould. When the magnesium ribbon fuse is ignited, the reaction.



starts producing tremendous amount of heat as a result of which the iron melts. This white hot molten iron is tapped from the crucible into the mould. The heated ends of the iron rods (to be welded) actually melt and mix with the molten metal added, giving a firm and strong weld.

## 14. Iron and Its Metallurgy

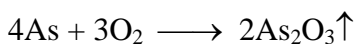
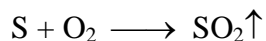
### 14.1 Concentration of Ore

#### Dressing of the ores

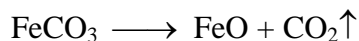
The iron ores are first broken into small pieces 3–5 cm in size.

#### Roasting or Calcination

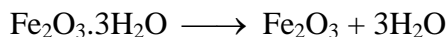
During roasting S, As, P are oxidised to the respective oxides.



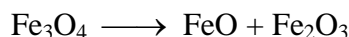
$\text{FeCO}_3$  decomposes as,



$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  loses water

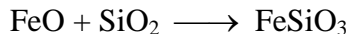


$\text{Fe}_3\text{O}_4$  is decomposed to ferrous oxide and ferric oxides.



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Ferrous oxide reacts with silica to form ferrous silicate at high temperature.



But the conversion of FeO into Fe<sub>2</sub>O<sub>3</sub> will prevent the formation of FeSiO<sub>3</sub>. Thus the mass of the ore becomes porous causing the increase in the effective surface area.

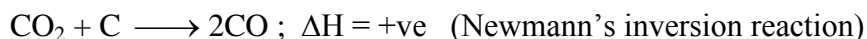
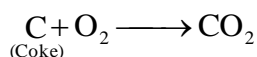
## Smelting in the Blast furnace

Blast furnace is a shaft furnace made of steel plate of 20–30 in with 4–4.6 diameter.

## 14.2 Extraction of Cast Iron

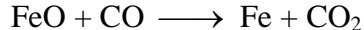
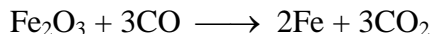
Iron is usually extracted from the haematite. Concentrated ore after calcination is reduced with carbon i.e. smelted in the blast furnace. Reactions taking place in the blast furnace are

### Zone of combustion

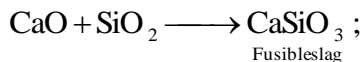
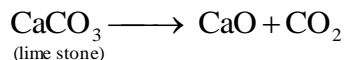


### Zone of reduction

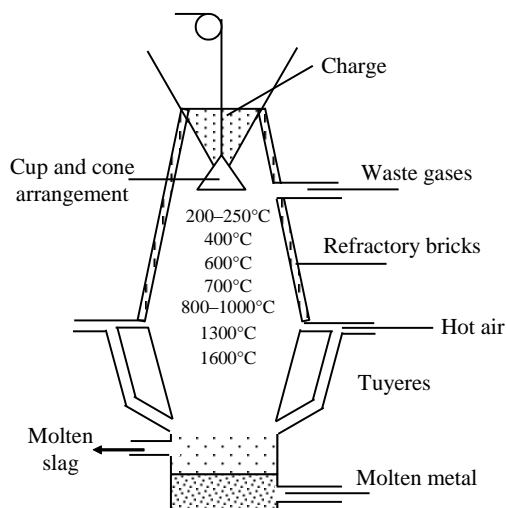
The following reduction reaction is called indirect reduction, which is done by CO, which is unstable at higher temperature (See Ellingham diagram).



### Zone of slag formation



### Zone of fusion (lower part of furnace)

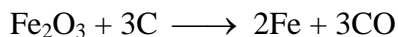


## METALLURGY

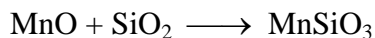
Molten iron is heavier than from molten slag. The two liquids are periodically tapped off. The molten iron tapped off from the furnace is solidified into blocks called 'plugs'.

### 14.3 Preparation of Wrought Iron

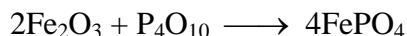
This is done by heating cast iron with haematite ( $\text{Fe}_2\text{O}_3$ ) which oxidises C to CO, S to  $\text{SO}_2$ , Si to  $\text{SiO}_2$ , P to  $\text{P}_4\text{O}_{10}$  and Mn to MnO



Where CO and  $\text{SO}_2$  escape, manganous oxides (MnO) and Silica ( $\text{SiO}_2$ ) combine to form slag.



Similarly phosphorus pentoxide combines with haematite to form ferric phosphate slag.



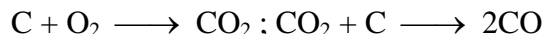
#### Bosh

The diameter of the furnace gradually increases from the top down wards. Widest part of the furnace is called Bosh. At above 2m tuyers are there through which hot air blast is blown into the furnace.

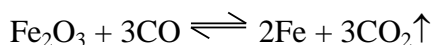
#### Hearth

Below the bosh this region exists. (1) slag notch is at higher height and (2) tap hole for metal passage at lower position from the bottom. At the top of the furnace the hopper is there which is cup and cone arrangement. Through this charge is introduced till the charge bed in the furnace is  $\frac{4}{5}$ <sup>th</sup> the of the furnace. Hot air at  $700^\circ\text{C}$  is forced into the furnace through the tuyers. The thermal gradient inside exists from  $1800^\circ\text{C}$  (hearth) to  $400^\circ\text{C}$ – $900^\circ\text{C}$  in the upper region. Near the both the temperature varies from  $1200^\circ$ – $1300^\circ$  chemical reactions which take place are:

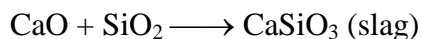
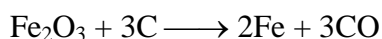
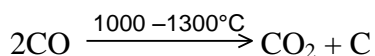
1. At  $1200^\circ\text{C}$  near the tuyers,



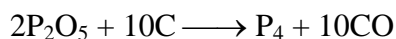
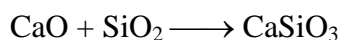
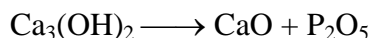
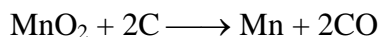
2. Above bosh  $600^\circ$  –  $900^\circ\text{C}$ , ferric oxide is partially reduced by CO as



3.  $\text{CaCO}_3 \xrightarrow{900^\circ\text{C}} \text{CaO} + \text{CO}_2$



4. The reaction at  $1500^\circ\text{C}$ ,  $\text{MnO}_2$  is reduced to Mn



5. **Collection of Cast Iron:** Metal is cast into ingots or in the ladle for further refining like steel making.

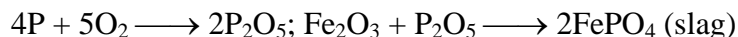
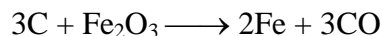
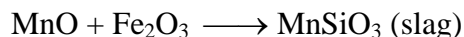
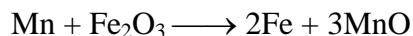
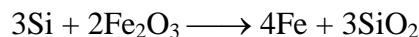
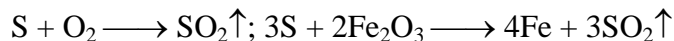
# METALLURGY

## Wrought Iron

Minimum % of carbon in wrought iron is 0.1 – 0.1% and other impurities like S, P, Mn, Si less than 0.3%.

## Manufacturing process

Cast iron is taken in puddling furnace and melted by hot blast of air. The chemical reactions, which occur, are



The impurities are removed from iron, the melting point of the metal rises and it becomes a semi solid mass. Metal taken out from the furnace in the form of balls with the help of the ruddles. The balls are then beaten under hammer to separate out the slag. The product thus formed is thus called wrought iron.

## Some Important Alloys of Iron

Sl. No.	Name	Composition
1.	Stainless steel	Fe, Cr, Ni
2.	Invar	Fe, Ni
3.	Alnico	Fe, Al, Ni, Co
4.	Brass	Cu, Zn
5.	Bronze	Cu, Zn, Sn
6.	Gun metal	Cu, Sn
7.	Bell Metal	Cu, Sn
8.	German Silver	Cu, Zn, Ni
9.	Solder, pewter	Pb, Sn
10.	Babbitt metal	Sn, Sb, Cu

## 15. Tin and Its Metallurgy

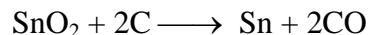
The chief ore of tin is cassiterite or tin stone,  $\text{SnO}_2$ . It also contains silica and wolframite (iron tungstate,  $\text{FeWO}_4$ ), iron pyrites and arsenical pyrites and sometimes copper pyrites. The ore is concentrated, and then smelted to give crude tin which is finally refined.

### 15.1 Roasting

The impure tin stone is roasted in current of hot air in an inclined revolving tube-furnace, when arsenic and sulphur are expelled as volatile oxides; most of the iron is converted to the magnetic oxide,  $\text{Fe}_3\text{O}_4$  and copper forms oxide and sulphate.

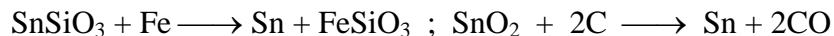
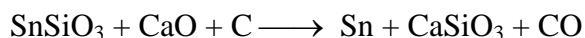
### 15.2 Smelting

The black tin is mixed with one-fifth of its weight of crushed anthracite coal and some lime and fluorspar to act as a flux and smelted at  $1200^\circ\text{--}1300^\circ\text{C}$  in a reverberatory furnace when the tin oxide is reduced to the metal. The molten tin and slag form two layers and are run out separately



The liquid tin is cast into ingots or else refined to a higher purity.

A good amount of tin goes into the slag, because of the amphoteric nature of tin dioxide. the slag may contain 10 to 25% tin. Tin is recovered from the slag by smelting it at a much higher temperature with carbon, flux and some scrap iron to decompose the tin oxide



### 15.3 Refining

- (i) The crude tin is refined by liquation or sweating i.e. by heating the ingots on the sloping hearth of a reverberatory furnace, when the easily fusible tin (melting point  $232^\circ$ ) melts and runs away leaving behind a dross of an alloy of tin with iron, copper, tungsten and arsenic. Bi and Pb because of their low melting points go with tin and remain in the sweated tin.
- (ii) The liquated tin is further treated by poling, i.e. the liquid tin stirred with poles of green wood so that a large surface is exposed to the air, when the remaining impurities are oxidised and separated as scum on the surface and are skimmed off. The tin so obtained is of over 99% purity. The scum and dross contain much tin and are worked up by smelting.

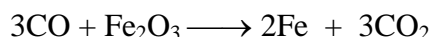
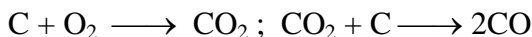
## Fundamental Solved Example

### Example 1.

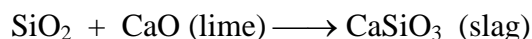
When the ore hematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel, but also produces a silicate slag that is useful in making building material such as cement. Discuss the same and show through balanced chemical equation.

### Solution:

Hematite ( $\text{Fe}_2\text{O}_3$ ) on burning with coke & lime at 2000°C results in following.



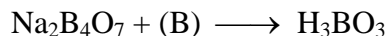
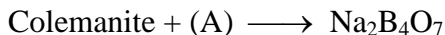
(Steel)



$\text{CaSiO}_3$ (slag) is used as the building material.

### Example 2.

Identify (A) and (B) in the following reactions:



### Solution:

(A) is sodium carbonate.



(B) is either concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ .



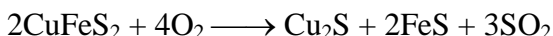
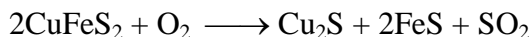
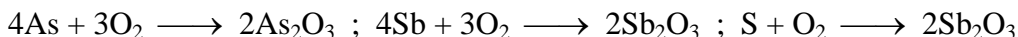
### Example 3.

Explain the following:

- (i) Partial roasting of sulphide ore is done in the metallurgy of copper.
- (ii) Zinc and not copper is used for the recovery of silver from complex  $[\text{Ag}(\text{CN})_2]^-$
- (iii) In the metallurgy of iron, lime–stone is added to the ore.

### Solution:

(i) The concentrated ore is roasted in reverberatory furnace in a current of air. The volatile impurities such as free sulphur, arsenic and antimony are removed as volatile oxides and the ore is partially oxidised.

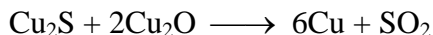


## METALLURGY

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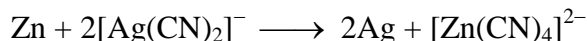


A mixture of sulphides and oxides is formed. The  $\text{Cu}_2\text{O}$  so formed reacts with unconverted  $\text{Cu}_2\text{S}$  to form copper.

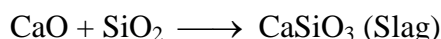
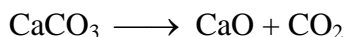


If  $\text{Cu}_2\text{S}$  is not present in the mixture, it will combine with flux and will go to slag, which is a loss of Cu.

(ii) Zinc is cheaper as well as stronger reducing agent in comparison to copper.



(iii) Lime stone is added as a flux. It is decomposed in the furnace into  $\text{CaO}$  and  $\text{CO}_2$ .  $\text{CaO}$  reacts with gangue silica and forms infusible slag,  $\text{CaSiO}_3$ .



### Example 4.

Explain the following:

- (i) Why is chalcocite roasted and not calcined in the extraction of copper?
- (ii) Magnesium oxide is used for the lining of steel making furnace.

### Solution:

- (i) Air is necessary to convert impurities such as sulphur, arsenic and antimony into volatile oxides and for partial oxidation of the pyrite ore. Calcination does not use oxygen while roasting is done in presence of air. Thus, roasting and not calcination is done in the metallurgy of copper.
- (ii) Magnesium oxide is used for the lining of steel making furnace in those steel making processes where slag is basic in nature. So, that lining cannot be destroyed.

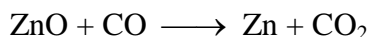
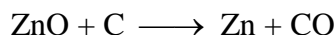
### Example 5.

Excess of carbon is added in zinc metallurgy. Explain.

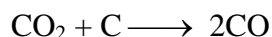
### Solution:

Carbon play two roles in the metallurgy of zinc.

- (a) It reduces zinc oxide to zinc.



- (b) It reduces  $\text{CO}_2$  into  $\text{CO}$ , which is used as a fuel.



### Example 6.

What is the role of carbon in blast furnace.

### Solution:

- (a) It acts as a reducing agent.
- (b) It acts as a spacer during smelting.