Metallurgy

1. METALLURGY

The chemistry of extracting metals from their ores is called metallurgy. The following steps are involved in the extraction of metals

(i) Concentration of ore

(ii) Conversion of concentrated ore into metal oxide

(iii) Conversion of metal oxide into metals

(iv) Purification of metal.

1.1 Concentration of ore

The metal ores obtained from mines are generally mixed with non metals, sand, lime, clay and rock materials. These impurities are known as gangue or matrix. The removal of impurities from the ore is called concentration of the ore. The common methods of concentration are as follows

[1] Gravity separation-

This separation is based on the fact that specific gravities of metallic ore and the earthy impurities are different. The finely powered ore is agitated with water or washed with a running stream of water on a willley table. The lighter impurities are washed away leaving behind ore particles on the table.

[2] Froth flotation process -

This method is generally applied to sulphide ores because sulphide ores are preferentially wetted by oils. The finely powdered ore is introduced into water to which small quantity of a suitable oil is added. Water is then agitated with a stream of air. The ore which is preferentially wetted by oil rises to the surface along with the foams while the gangue which is preferentially wetted by water remains in the water in the bottom. The foam along with ore is separated. This process is called froth flotation process.

In froth flotation two types of substances are used - Frothing agent and flotation agent. Pine oil and eucalyptus oil are generally used as frothing agents and sodium ethyl xanthate or sodium amyl xanthate as flotation agents.

[3] Electromagnetic separation -

This method is used only when impurities present or the metallic ore are magnetic in nature. The finely powdered ore is dropped over electromagnetic rollers. At the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller while non magnetic impurities fall away from the roller.

[4] Chemical method or leaching -

This method depends upon the chemical nature of the ore. For example bauxite ore of aluminium contains the impurities of iron oxide, titanium oxide and silica etc. Bauxite is heated in a solution of NaOH at 150-200°C. It dissolves in the solution forming a soluble complex while the impurities remain insoluble which are removed by filtration.

$$Al_2O_3 + 6NaOH \rightarrow \underset{\text{Sodium aluminate}}{2Na_3AlO_3} + 3H_2O$$

The filtrate is boiled with water, aluminium hydroxide gets precipitated which on heating at high temperature changes to alumina.

$Na_3AlO_3 + 3H_2O \rightarrow Al(OH)_3 + 3NaOH$; $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

1.2 Conversion of concentrated ore into metal oxide

[1] Calcination-

It is a process in which the concentrated ore is heated to expel the organic matter and moisture present in the ore. The ores are heated in the absence of air below their melting point. Ores are converted to metal oxide. This process is also used to remove water from hydrated hydroxide ores and carbon dioxide from carbonate ores. The process is generally carried out in reverberatory furnace. It renders the ore porous.

$$CaCO_3 \rightarrow CaO + CO_2$$

Lime stone

$$Al_2O_3.2H_2O \text{ (Bauxite)} \rightarrow Al_2O_3 + 2H_2O$$

$$2Fe_2O_3.3H_2O \text{ (Limonite)} \rightarrow 2Fe_2O_3 + 3H_2O$$

[2] Roasting -

This process is generally done with sulphide ores. Sulphide ores alone or in the presence of other substance are heated in the presence of air below their melting points. The impurities like sulphur, arsenic, phosphorus etc. are removed in the form of their volatile oxides. This process is generally carried out in reverberatory furnace or blast furnace.

$$2ZnS \text{ (Zinc blende)} + 3O_2 \rightarrow 2ZnO + 2SO_2 \uparrow$$

$$2PbS \text{ (Galena)} + 3O_2 \rightarrow 2PbO + 2SO_2 \uparrow$$

1.3 Conversion of metal oxide into metal

[1] Carbon reduction method

Smelting - The roasted or calcinated ore is mixed with suitable quantity of coke, the reducing substance and the flux and heated to a high temperature above the melting point of the metal. The metal oxide reduces to metal and the flux combines with impurities (gangue) to form easily fusible product known as slag. Slag is not soluble in molten metal. It is lighter and can be easily skimmed off from the surface of the molten metal. This process is done in reverberatory furnace or blast furnace.

$$\underset{\text{Tin oxide}}{SnO_2} + 2C \rightarrow \underset{\text{Tin}}{Sn} + 2CO \uparrow$$

$$PbO \text{ (Lead oxide)} + C \rightarrow Pb + CO \uparrow$$

$$ZnO \text{ (Zinc oxide)} + C \rightarrow Zn + CO \uparrow$$

Flux -

Metal ore contains some acidic or alkaline impurities which can form fusible products by combining with some substances. These substances are added during smelting and are called flux. The fusible product is called slag. For acidic impurity basic flux is used and for basic impurity acidic flux is' used.

$$\underset{\substack{\text{Basic}\\\text{flux}}}{CaO} + \underset{\substack{\text{Acidic}\\\text{impurity}}}{SiO_2} \rightarrow \underset{\substack{\text{Calcium silicate}\\\text{slag}}}{CaSiO_3}$$

$$\underset{\substack{\text{Basic}\\\text{impurity}}}{MnO} + \underset{\substack{\text{Acidic}\\\text{flux}}}{SiO_2} \rightarrow \underset{\substack{\text{Manganese silicate}\\\text{slag}}}{MnSiO_3}$$

$$\underset{\substack{\text{Basic}\\\text{impurity}}}{FeO} + \underset{\substack{\text{Acidic}\\\text{flux}}}{SiO_2} \rightarrow \underset{\substack{\text{Iron silicate}\\\text{slag}}}{FeSiO_3}$$

Slag is generally a silicate or phosphate and melt before the melting point of the metal.

[2] Aluminio thermic process - (Goldschmidt thermite process) -

A mixture of metal oxide and aluminium powder (thermite) is ignited in a closed crucible by means of a lighted magnesium ribbon having ignition mixtures ($Mg + BaO_2$) at one end. This is an exothermic reaction. The temperature of the crucible reaches to 3000°C. At this temperature metal oxide is reduced to metal by aluminium.

$$Cr_2O_3 + 2Al \rightarrow 2C + Al_2O_3$$

$$3Mn_3O_4 + 8\ Al \rightarrow 9Mn + 4Al_2O_3$$

[3] Precipitation method-

More reactive element (more electropositive) replaces the less reactive (less electropositive) element from its salt solution. For *e.g.* iron can precipitate Cu from copper sulphate solution while copper can not precipitate iron from iron sulphate solution. This principle is used in the precipitation method. Silver can be extracted from its ores by using this theory.

If zinc is added to a solution of silver, silver precipitates out.

$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$

Silver glance Sodium argentocyanide

$2Na[Ag(CN)_2] + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$

[4] Electrolytic method -

If metal oxides, chlorides or hydroxides in fused state are electrolyzed the metals deposit at cathode. The reduction of active elements such as alkali metals, alkaline earth metals and the oxides of Al with carbon is difficult because these form carbides with carbon at high temperature.

1.4 Purification

Metals can be purified by following methods

[1] Distillation - The metals with low boiling points can be purified by distillation.

Examples - Zn, Cd, Hg etc.

[2] Liquation - This process is used when the impurity is less fusible than the metal itself. The impure metal is placed on the slopping hearth of the furnace and heated. The metal melts and drains away leaving behind the impurities. For *e.g.* tin.

[3] Oxidation method - This method is employed when the inpurity have greater affinity with oxygen as compared to metal. The impurities are oxidized to form scum. The scum is skimmed off. Some times metal oxides are used as oxidizing agents. For *e.g.* copper oxide is added to impure copper.

[4] Electrolysis -

Most of the metals are purified electrolytically. The metal salt is taken as electrolyte, impure metal rod as anode and thin pure metal rod or strip as cathode. On electrolysis pure metal is deposited at cathode. Cu, Ag, AI, Zn, Cr etc. metals are purified by this method.

2. Extraction of Copper, Cu

(i) Copper was named as cuprous by Romans because they obtained it from Cyprus island.

(ii) It is also found in small quantity in pea, peacock feather and animal blood.

(iii) **Occurrence -** It is found in nature in both free and combined state.

The Important ores of copper are

[1] Cuprite or ruby copper or cuprite red Cu_2O

[2] Copper pyrite (Chalcopyrites) $CuFeS_2$ or $Cu_2S.Fe_2S_3$

[3] Copper glance Cu_2S

[4] Malachite $Cu(OH)_2.CuCO_3$

(e) Azurite $Cu(OH)_2.2CuCO_3$ 76% of the copper is extracted from the ore copper pyrites.

(iv) Indian Sources-

Bihar (Singhbhum), Andhra Pradesh, Karnataka (Mysore), Sikkim, Orissa, Rajasthan (Khetri and Dariba). In India Copper is extracted by Hindustan Copper Ltd.

(v) Extraction of Copper from Copper pyrites

[1] Concentration -

The ore is concentrated by froth flotation method. .

[2] Roasting -

This process is done in reverberatory furnace. The Impurities of arsenic and antimony are removed as volatile oxides. Sulphur oxidises to SO_2.

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2 \uparrow \text{ (Main)}$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow \text{ (Side)}$$

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \uparrow \text{ (Side)}$$

[3] Smelting –

Coke and sand is mixed with roasted ore and it is smelted in blast furnace. Cu_2S and FeS are oxidised fastly. FeO reacts with SiO_2 to give slag ferrous silicate.

$$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (slag)}$$

Cu_2O obtained in roasting reacts with FeS to give cuprous sulphide and FeO. This FeO again reacts with SiO_2 to give slag $FeSiO_3$

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

$$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (Slag)}$$

This slag is removed.

Molten Cu_2S and a small amount of FeS remains below the surface of slag. This mixture is called matte. It is taken out from the furnace.

[4] Bessemerisation -

Molten matte *i.e.* mixture of Cu_2S and FeS is transferred to a Bessemer converter. Bessemer converter is a pear shaped furnace in which the inner lining is of CaO. or MgO. A blast of air mixed with sand is blown through the molten matte. The following reactions take place

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow$

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2\uparrow$

The molten copper thus obtained is cast into ingots. It is about 98% pure copper. It is called blister copper because of blistered appearance due to escape of SO_2 gas during the cooling of molten copper. This copper contains about 2% mixture of Ag, Au, Ni, Zn, Pb and Sn. etc.

(e) Refining - (i) Poling - The blistered copper is heated in the reverberatory furnace. Cuprous oxide present in it oxidises the impurities. The impurities of sulphur and arsenic separate as volatile oxides and the other impurities as slag. This copper still has the impurity of cuprous oxide. The molten copper is then agitated with green wood bamboos. Cuprous oxide is reduced to copper by the hydrocarbons obtained from the green wood bamboos.

(ii) Electrolytic refining

Anode - Blistered copper

Cathode - Pure copper

Electrolyte - Aqueous solution of copper sulphate.

On electrolysis

At cathode - $Cu^{2+} + 2e^- \rightarrow Cu$

At anode – $Cu \rightarrow Cu^{2+} + 2e^-$

3. Extraction of copper from oxide or carbonate ores

[1] Concentration-

Gravity separation method is employed.

[2] Calcination -

On calcination the volatile impurities are removed and the following reactions take place

$$CuCO_3 \rightarrow CuO + CO_2$$

$$Cu(OH)_2 \rightarrow CuO + H_2O$$

[3] Smelting- Calcinated ore is smelted by mixing the suitable flux

$$Cu_2O + C \rightarrow 2Cu + CO \uparrow$$

$$CuO + C \rightarrow Cu + CO \uparrow$$

[4] Purification - Electrolytic refining.

4. Alloys of Copper

(i) Brass - Cu, 60-80% and Zn, 40-20%

(ii) Bronze - Cu, 75-90% and Sn, 25-10%

(iii) Aluminium bronze– Cu 90% and Al 10%

(iv) Monel Metal– Cu 30%, Ni, 67% and Fe + Mn, 3%

(v) Bell Metal – Cu, 80% Sn, 20%

(vi) Gun metal– Cu, 87%: Sn, 10%; Zn, 3%

(vii) German Silver – Cu, 50%, Zn 25%; Ni 25%

(viii) Phosphorus bronze– Cu 85%, Sn 13%, P 2%

5. Extraction of silver

(i) Occurrence

Silver is found in free and combined state both, In free state it is generally found in Mexico, Canada, and USA. In alluvial sand, it is found with gold and copper. Its important ores are

[1] Argentite or silver glance- Ag_2S

[2] Pyrargyrite or ruby silver- Ag_2S, Sb_2S_3

[3] Horn silver- AgCl,

[4] Copper silver glance – $Cu_2S.Ag_2S$

(e) Stiphenite - Ag_5SbS_4

(f) Argentiferrous galena (PbS) - It contains about 0.01 to 0.1% silver.

(g) Silver can also be prepared from the anode mud obtained in the extraction of copper.

(ii) Indian sources - Colar and Hatti (Karnataka) and Jawar mines (Rajasthan)

(iii) Extraction of silver from its ores –

[1] Cyanide process or Mac Arthur forest process

(i) Concentration - Froth flotation process.

(ii) Concentrated ore is reacted with dilute solution of sodium cyanide and the mixture is agitated with air. Silver forms a soluble complex,

$$\underset{\text{Free silver}}{4Ag} + 8NaCN + 2H_2O + O_2 \rightarrow \underset{\text{Sodium argentocyanide}}{4Na[Ag(CN)_2]} + 4NaOH$$

$$AgCl\ (\text{Horn silver}) + 2NaCN \rightarrow Na[Ag(CN)_2] + NaCl$$

$$Ag_2S\ (\text{Silver glance}) + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + 2H_2O + 5O_2 \rightarrow 2Na_2SO_4 + 4NaOH + 2S$$

The solution is filtered. Filtrate contains sodium argentocyanide.

(iii) On addition of zinc powder, in sodium argentocyanide solution, silver precipitates out.

$2Na[Ag(CN)_2] + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$

(iv) Silver precipitate is filtered and dried. It is then fused with borax or potassium nitrate for purification.

[2] Amalgamation process

Silver ore + Salt + roasted pyrites mixture is finely powdered. Salt + roasted pyrite form ferric chloride which reacts with silver ore.

$$Ag_2S\ (\text{Silver glance}) + FeCl_3 \rightarrow 2AgCl + 2FeCl_2 + S$$

$$2AgCl + 2Hg \rightarrow Hg_2Cl_2 + 2Ag$$

Silver chloride thus formed reacts with mercury to give silver which forms silver amalgam in the excess of mercury. On distillation of amalgam mercury distills out and silver remains in the container.

[3] From Argentiferrous lead

The concentration of silver in argentiferrous lead can be increased by the following methods.

(i) Parkes process -

In the molten argentiferrous lead, a small amount of molten zinc is added. The mixture is shaken well. Silver forms an alloy with zinc which on cooling solidifies and is skimmed off while the lead still remains in the molten state. On distillation of this alloy, zinc distills out and silver remains in the container. This silver contains the impurity of lead.

(ii) Pattinson's process -

This method is based on phase rule. When molten argentiferrous lead is allowed to cool slowly, lead crystals separate out. This process is repeated many times until the concentration of silver in the mixture rises to 2.5% when entire mass solidifies.

From the concentrated lead silver mixture, silver is removed by cupellation.

(iii) Cupellation -

The impure silver is heated in a small bone-ash crucible (cupel) in a blast of air in a small reverberatory furnace. Lead gets oxidised to litharge (PbO) which is blown away.

Purification - Silver so obtained is further purified by electrolytic method.

Anode - Impure silver

Cathode - Pure silver

Electrolyte - $AgNO_3$ soln. + 1 %HNO_3 On passing the current -

At anode - $Ag \rightarrow Ag^+ + e$

At cathode - $Ag^+ + e^- \rightarrow Ag$

6. Silver from Coins and Ornaments

(i) Coins and ornaments contain the impurity of Cu and Ni.

(ii) These coins and ornaments' are treated with HNO_3, A mixture of nitrates of Ag, Cu and Ni is obtained.

(iii) On addition of HCl to this solution, a white precipitate of AgCl is formed which is filtered out.

(iv) This precipitate of AgCl can be converted to Ag by anyone of following methods.

[1] Fusing with the excess of Na_2CO_3 – $4AgCl + 2Na_2CO_3 \rightarrow 4Ag + 4NaCl + 2CO_2 + O_2$

[2] Reducing with Zn + conc. H_2SO_4 – $Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$

$$AgCl + H \rightarrow Ag + HCl$$

[3] Reducing with alkaline glucose

$$2AgCl + 2NaOH \rightarrow Ag_2O + 2NaCl + H_2O$$

$$\underset{\text{Glucose}}{Ag_2O + C_6H_{12}O_6} \rightarrow \underset{\text{Gluconic acid}}{2Ag + C_6H_{12}O_7}$$

Silver thus obtained is fused with borax or KNO_3 for further purification. It is again purified by electrolytic method.

7. Extraction of aluminium

(i) Wholler prepared aluminium by the reaction of potassium metal with anhy. $AlCl_3$ Bunsen and Deville prepared it from the reaction of $NaAlCl_4$ with sodium and also from the electrolysis of $NaAlCl_4$ Charles M. Hall prepared aluminium from fused cryolite.

(ii) Occurrence-Aluminium is. found in nature only in combined state. Its important ores are

[1] Felspar - $KAlSi_3O_8$

[2] Mica (Abhrak) - $KH_2Al_2(SiO_3)_4$

[3] Kaolin - $Al_2O_3.2SiO_3.2H_2O$

[4] Corundum - Al_2O_3

(e) Diaspore - $Al_2O_3.H_2O$

(f) Bauxite - $Al_2O_3 . 2H_2O$

(g) Cryolite-Na_3AlF_6

(h) Alunite or alumstone – $K_2SO_4. Al_2(SO_4)_34Al(OH)_3$

(i) Thrquoise - $AlPO_4.Al(OH)_3$- H_2O

(j) Gibbsite-$Al_2O_3.3H_2O$

(k) Beryl - $3BeO. Al_2O_3. 6SiO_2$.

Indian sources - Mainly bauxite ore is found in India. It is found in U .P., M.P. Gujrat, Tamilnadu, orissa, Bihar and

J and K. The production of aluminium is carried out by Indian aluminium company Alvai, Madras aluminium Co. Madras and Hindustan aluminium U.P.

Extraction of aluminium from bauxite Purification of bauxite

[1] Baeyer' process-

Finely powdered bauxite is digested with an aqueous solution of sodium hydroxide in an autoclave at 150° C and 80 atmospheric pressure. Alumina present in bauxite dissolves as sodium meta aluminate. The' other impurities remain insoluble and are filtered out.

$$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

The filtrate containing sodium metaaluminate is agitated with. freshly precipitated $Al(OH)_3$ for 36 hrs. Sodium meta aluminate hydrolyses to $Al(OH)_3$, $NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$, $Al(OH)_3$ thus obtained is filtered, washed, dried and heated at about 1500°C. Alumina is obtained.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

[2] Hall's method -

Bauxite ore is. fused with Na_2CO_3 and the sodium meta aluminate' formed is extracted with water.

$$Al_2O_3.2H_2O + Na_2CO_3 \rightarrow 2NaAlO_2 + 2H_2O + CO_2 \uparrow$$

CO_2 gas is passed through the sodium meta aluminate solution at 50-60°C $Al(OH)_3$ gets precipitated. .

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow 2Al(OH)_3 + Na_2CO_3$$

$Al(OH)_3$ thus obtained is filtered, dried and heated in a furnace at about 1500°C to obtain Al_2O_3

[3] Serpek's process - This process is used when bauxite contains relatively a large amount of silica as impurity. Bauxite is heated with carbon at 1800°C in the current of N_2. AlN is formed.

$$Al_2O_3.2H_2O + 3C + N_2 \rightarrow 2AlN + 3CO + 2H_2O$$

Aluminium nitride on hydrolysis gives $Al(OH)_3$ which on heating at 1500°C gives Al_2O_3

$$2AlN + 6H_2O \rightarrow 2Al(OH)_3 + 2NH_3$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

(ii) Electrolytic reduction of alumina-

Pure. Al_2O_3 on electrolytic reduction gives aluminium.

The melting point of Al_2O_3 is about 2000°C. This is reduced by mixing fused cryolite (Na_3AlF_6) + fluorspar (CaF_2) to it. The melting point of this mixture is about 900°C. This mixture. is good conductor of electricity. The inner carbon lining of the cell is used as cathode and the carbon rods as anode.

The fused mixture of alumina + Cryolite + Fluorspar is taken in the cell whose temperature is maintained at about 900 to 1000°C. This mixture is covered by carbon powder which maintains the temperature of the cell. The carbon anodes are dipped in the mixture. Aluminium gets free at cathode while oxygen at anode. Aluminium thus obtained is about 99.8% pure.

Purification of aluminium

Hoope's method - Aluminium is refined electrolytically. The refining cell consists of three fused layers - (i) The bottom anode layer of impure Al + Cu + Si, (ii) The middle electrolyte layer of cryolite (Na_3AlF_6) + BaF_2 and (iii) The top cathode layer of pure aluminium. On passing the electric current, pure Al from the bottom layer rises to the upper layer.

Alloys of aluminium

(i) Magnelium - Al 95%, Mg 5%

(ii) Duralium - Al 95%, Cu 4%, Mg 0.5%, Mn 0.5%

(iii) Y-alloy - Al 93%, Cu 4%, Ni 2%, Mg 1%

8. Extraction of iron

(i) The important ores of iron are

[1] Haematite-Fe_2O_3	[2] Magnetite-Fe_3O_4
[3] Limonite-$Fe_2O_3 . 3H_2O$	[4] Siderite - $FeCO_3$
(e) Iron pyrites - FeS_2	(f) Copper pyrites - $CuFeS_2$
(g) Arsenickle pyrites - FeAsS	(h) Vivianite- $Fe_3(PO_4)_2 . 8H_2O$

(ii) Indian sources

The main ores of iron is hematite in india. It is found in Singhbhum, Mysore, Durg" Chand, Mayurbhanj. Steel plants are located at J amshedpur, Asansol, Bhadravati, Bhilai, Durgapur, Bokaro and Rourkela.

(iii) Various forms of iron

[1] **Cast iron or pig iron-** It is least pure form of iron containing about 2.2 to 4.4% carbon. It is brittle and can not be hammered.

[2] **Wrought or malleable iron -** It is the purest form of iron containing about 0.1 to 0.25% carbon. It is malleable.

[3] **Steel-** It comes in between cast iron and wrought iron and contains about 0.25 to 2.0% carbon. It is malleable. Its properties depend upon the quantity of carbon present.

Extraction of cast iron

(i) Concentration of ore – Iron ores are concentrated by magnetic separation method.

(ii) Hematite and magnetite after concentration can be used directly. Sulphide ore is first roasted and carbonate ore is calcined.

(iii) **Smelting-** In calcined or roasted ore, coke (reductant) and lime stone (Flux) is mixed in appropriate proportion. This mixture is smelted in a blast furnace. The following reactions take place

$$[1]\ C + O_2 \rightarrow CO_2 \uparrow, \Delta H = -97 \text{ kcal}$$

$$1500°C$$

$$[2]\ CO_2 + C \rightarrow 2CO \uparrow, \Delta H = 58 \text{ kcal}$$

[3] At 400-700°C in the reduction region, the following reactions occur –

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \uparrow$$

This reaction takes place in the following steps

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \uparrow$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \uparrow$$

$$FeO + CO \rightarrow Fe + CO_2 \uparrow$$

Iron thus obtained is in solid state and becomes porous. It is known as spongy iron.

[4] At 1000°C, silica present in ore combines with CaO obtained from lime stone to give slag $CaSiO_3$.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

$$CaO + SiO_2 \rightarrow CasiO_3 \text{ (Slag)}$$

(e) At 1300°C, spongy iron melts and absorb. C, P, SiO_2 etc. Slag also melts at this temperature. Both fall at the bottom of the furnace. The molten metal obtained from the furnace is called pig iron. It contains 2.6-4.3% of carbon and varying amounts of Mn, Si, Sand P.

White cast iron - If the molten iron obtained from blast furnace is suddenly cooled, the carbon is present in the form of cementite (Fe_3C) and the white coloured cast iron is obtained.

Grey cast iron - If the molten iron obtained from blast furnace is cooled slowly, the most part of carbon is present in the form of graphite and the grey coloured cast iron is obtained.

Cast iron is not rusted. Its melting point is about 250ºC less than the pure iron.

Wrought iron

It is obtained by purifying cast iron by the process known as pudding. The cast iron is. heated on the hearth of a reverberatory furnace lined with hematite (Fe_2O_3) or magnetite (Fe_3O_4). The impurities of C, Si, P, Mn, etc. are oxidised.

$$3C + Fe_2O_3 \rightarrow 2Fe + 3CO \uparrow$$
$$3Si + 2Fe_2O_3 \rightarrow 4Fe + 3SiO_2$$
$$3Mn + Fe_2O_3 \rightarrow 2Fe + 3MnO$$
$$6P + 5Fe_2O_3 \rightarrow 10Fe + 3P_2O_5$$

P_2O_5 forms slag ferric phosphate with hematite.

$$P_2O_5 + Fe_2O_3 \rightarrow 2FePO_4$$

After separation of slag, the iron is taken out in the form of balls and the slag squeezed out by hammering. Wrought iron thus obtained retains about 0.2% C and traces of P and Si etc. in the form of slag. The presence of slag gives strength and toughness to metal and make it resistant towards rusting.

9. Steel

It can be made as follows

(i) By reducing the amount of carbon in cast iron.

(ii) By adding some carbon to wrought iron.

(iii) By mixing the required amounts of cast iron and wrought iron.

(iv) Directly from ore.

Generally steel is prepared from cast iron.

Production of steel from cast iron–

(i) Acidic Bessemer process

[1] The Bessemer is lined with silica.

[2] In the acidic Bessemer, hot air oxidise Mn, Si and C impurities present in the cast iron.

$$2Mn + O_2 \rightarrow 2MnO$$
$$Si + O_2 \rightarrow SiO_2$$
$$2C + O_2 \rightarrow 2CO \uparrow$$

[3] MnO combines with SiO_2 to give slag $MnSiO_3$ which is separated. Carbon is oxidised to carbon monoxide which burns with a blue flame at the mouth of converter.

[4] When the whole of the carbon is oxidised the blue flame suddenly stops.

The requisite amount of carbon is then added usually in the form of an alloy of Fe + Mn + C, Called spiegel. The process is called spiegeleisen. The resulting product is manganese steel which is harder and possesses much greater tensile strength.

(ii) Basic Bessemer process –

[1] This process is used when cast iron contains comparatively the higher impurity of phosphorus.

[2] The Bessemer is lined with CaO or MgO.

[3] Cast iron and lime stone are taken in the Bessemer and hot air is passed through them. Mn, Si, C and, P oxidise as

$$2Mn + O_2 \rightarrow MnO$$
$$Si + O_2 \rightarrow SiO_2$$
$$MnO + SiO_2 \rightarrow \underset{\text{Slag}}{MnSiO_3}$$
$$4P + 5O_2 \rightarrow 2P_2O_5$$
$$2C + O_2 \rightarrow 2CO \uparrow$$
$$3CaO + P_2O_5 \rightarrow \underset{\text{Slag}}{Ca_3(PO_4)_2}$$

$Ca_3(PO_4)_2$ is known as Thomas slag and is used as valuable fertilizer.

[4] Iron thus obtained undergoes spiegeleisen and steel is obtained.

(iii) Siemen's Martin open hearth process

[1] Iron. ore hematites used for the oxidation of impurities.

[2] Scrap steel, wrought iron of low quality is added to reduce the quantity of carbon.

[3] Heat is reproduced for obtaining the high temperature.

[4] The hearth of the furnace is lined with silica or dolomite. (CaO. MgO) depending upon the nature of the impurities.

(e) C, S, P, Si, and Mn are oxidised by hematite as

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \uparrow$$

$$2Fe_2O_3 + 3S \rightarrow 4Fe + 3SO_2 \uparrow$$

$$10Fe_2O_3 + 3P_4 \rightarrow 20Fe + 6P_2O_5$$

$$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2$$

$$Fe_2O_3 + 3Mn \rightarrow 2Fe + 3MnO$$

CO and SO_2 come out and other oxides form slag as follows which are separated.

$$MnO + SiO_2 \rightarrow \underset{\text{slag}}{MnSiO_3}$$

$$CaO + SiO_2 \rightarrow \underset{\text{slag}}{CaSiO_3}$$

$$3CaO + P_2O_5 \rightarrow \underset{\text{slag}}{Ca_3(PO_4)_2}$$

10. Alloys of steel

	Alloys	**Composition**
1.	Chrome steel	2-4%Cr, 98-96% Fe
2.	Tungsten steel	10-20% W, 90-80% Fe
3.	Stainless steel	12-14% Cr, 88-86% Fe or 2-4% Ni + 86-82% Fe
4.	Manganese steel	10-18% Mn, 90-82% Fe
5.	Nickel steel	3-5% Ni, 97-95% Fe
6.	Vanadium steel	0.2-1% V
7.	Invar	36% Ni, 64% Fe

11. Heat Treatment of Steels:

The hardness and elasticity of steel can be controlled by proper heat treatment.

Annealing - If steel is heated to redness and then allowed to cool slowly. it becomes malleable, soft and pliable. This operation is called annealing.

Hardening - If steel is heated to redness and is suddenly quenched by plunging into water or oil, it becomes extremely hard and brittle. This process is called hardening.

Tempering - Hard steel is heated up to 270°C and then allowed to cool slowly. It becomes' comparatively less hard and less brittle.

12. Important Ores of various metals

Manganese

(i) Pyrolusite - MnO_2
(ii) Manganite - $Mn_2O_3.H_2O$
(iii) Braunite - Mn_2O_3

Zinc

(i) Zinc blende - ZnS
(ii) Calamine - $ZnCO_3$
(iii) Zincite - ZnO
(iv) Franklinite - ZnO .Fe_2O_3

Mercury - Cinnabar - HgS

Calcium

(i) Limestone - $CaCO_3$
(ii) Gypsum-$CaSO_4.2H_2O$
(iii) Fluorspar - CaF_2
(iv) Phosphorite - $Ca_3(PO_4)_2$

Magnesium

(i) dolomite ~ $MgCO_3.CaCO_3$
(ii) Magnesite-$MgCO_3$
(iii) Epsomite-$MgSO_4.7H_2O$
(iv) Carnallite - $KCl.MgCl_2.6H_2O$
(v) Kieserite-$MgSO_4.H_2O$
(vi) Asbestos- $CaMg_3(SiO_3)_4$

Lead

(i) Galena - PbS
(ii) Anglesite - $PbSO_4$
(iii) Cerussite - $PbCO_3$

Tin- Cassiterite (Tin stone)-SnO_2

13. Names and formulae of some Compounds-

[1] Washing Soda-$Na_2CO_3.10H_2O$.
[2] Baking soda-$NaHCO_3$
[3] Common salt-NaCl
[4] Glauber's salt-$Na_2SO_4.10H_2O$
(5) Hypo salt-$Na_2S_2O_3.5H_2O$
(6) Chili salt petre-$NaNO_3$
(7) Nitre or Indian salt petre - KNO_3
(8) Salt cake-Na_2SO_4
(9) Salammoniac (Nausadar) - NH_4Cl
(10) Rock phosphate (Bone ash) $Ca_3(PO_4)_2$
(11) Mohr's salt - $FeSO_4(NH_4)_2SO_4.6H_2O$
(12) Calomel- Hg_2Cl_2
(13) Corrosive sublimate - $HgCl_2$
(14) Philosopher's wool-ZnO
(15) Blue vitrol-CuSO4.5H2O
(16) Green vitriol- $FeSO_4$. $7H_2O$
(17) Lunar caustic - $AgNO_3$
(18) White vitrol-ZnSO4.7H2O
(19) Litharge-PbO
(20) White lead-$Pb(OH)_2.2PbCO_3$
(21) Red lead-Pb_3O_4
(22) Chrome red - $PbO.PbCrO_4$
(23) Chrome yellow-$PbCrO_4$.
(24) Chrome alum - $KCr(SO_4)_2.12H_2O$
(25) Plaster of Paris-$CaSO_4.\frac{1}{2}H_2O$
(26) Lithopone-$BaSO_4$ + ZnS
(27) Microcosmic salt-$Na(NH_4)HPO_4$. $4H_2O$
(28) Hydrolith - CaH_2
(29) Pink salt - $(NH_4)_2SnCl_6$
(30) Laughing gas-N_2O
(31) Spodumene - $LiAl(SiO_3)_2$
(32) Nitrolium - $CaCN_2$
(33) Ferric alum-$NH_4Fe(SO_4)_2.12H_2O$

1. IMPORTANT ORES

Oxide Ore	ZnO	Zincite
	MnO_2	Pyrolusite
	SnO_2	Cassiterite
	Cu_2O	Cuprite
	Fe_2O_3	Hematite
	$Al_2O_3.2H_2O$	Bauxite
	$FeO.Cr_2O_3$	Chromite
	Fe_3O_4	Magnetite
	$Fe_2O_3.3H_2O$	Lymonite
	$3BeO.Al_2O_3.6SiO_2$	Beryl
Sulphide Ore	ZnS	Zinc Blende
	HgS	Cinabar
	PbS	Galena
	Ag_2S	Argentite or Silver glance
	FeS_2	Iron pyrites
	$CuFeS_2.CuS.FeS$	Copper pyrites
	$Cu_2S. Ag_2S$	Copper silver glance
	$Ag_2S.Sb_2S_3$	Pyrargyrites, Rubi silver
	Ag_5,SbS_4	Stifenite
	$FeAsS$	Arsenickel Pyrites
Halide Ore	$NaCl$	Rock Salt
	$AgCl$	Horn Silver
	CaF_2	Flour Spar
	$AlF_3.3NaF$	Cryolite
	$KCl\ MgCl_2.6H_2O$	Camelite
Carbonate Ore	$MgCO_3$	Magnesite
	$CaCO_3$	Lime stone
	$MgCO_3.CaCO_3$	Dolomite
	$ZnCO_3$	Calamine
	$PbCO_3$	Cerusite
	$FeCO_3$	Siderite
	$CuCO_3.Cu(OH)_2$	Malachite
	$2CuCO_3.Cu(OH)_2$	Azurite
	$SrCO_3$	Strontianite
Sulphate Ore	$BaSO_4$	Barytes
	$PbSO_4$	Anglisite
	$CaSO_4.2H_2O$	Gypsum
	$MgSO_4.7H_2O$	Eypsomite
	$SrSO_4$	Celestine
	$K_2SO_4.Al_2(SO_4)_3.24H_2O$	Alum
	$K_2SO_4.Al_2(SO_4)_3.4Al\ (OH)_3$	Alunite or Alumstone

Silicate Ore	$LiAl(SiO_3)_2$	Spodumene	
	$KAl Si_3O_8$	Felsper	
	Al2O3.2SiO2.2H2O		Caolin
		(or China-Clay)	
	$3BeO.Al_2O_3.6SiO_2$	Beryl	
	$CaO.3MgO.4SiO_2$	Asbestus	
	K2O.3Al2O3.6SiO22H2O	Mica	
	KH2.Al3.(SiO3)4		
Nitrate Ore	$NaNO_3$	Chili-Salt Peter	
	KNO_3	Salt peter or Indian salt peter	
Phosphate Ore	$Ca_3(PO_4)_2$	Rock Phosphate	
	$Fe_3(PO_4)_2.8H_2O$	Vivianite	
	$AlPO_4.Al(OH)_3.H_2O$	Terguoise	

2. FAMOUS PROCESS AND RELATED METAL

Poling	Cu
Perkes Process	Ag
Pattinson process	Ag
Cupellation process	Ag
Baeyer's Process	Al
Serpek's process	Al
Hall's process	Al
Siemens Martin open halth furnace	Fe
L.D. Process	Fe
Temperine	Fe

CHIEF ORES OF ALUMINIUM

Bauxite	$Al_2O_3.\ 2H_2O$
Diaspore	$Al_2O_3.\ H_2O$
Cryolite	$AlF_3.\ 3NaF$ or Na_3AlF_6
China clay/Caolin	$Al_2O_3.\ 2SiO_2.\ 2H_2O$
Mica	$K_2O.\ 3Al_2O_3.\ 6SiO_22H_2O$
Felspar	$KAlSi_3O_8$
Corundum/Ruby/Sapphire/emerald / Topaz	Al_2O_3
Gibbsite	$Al_2O_3.\ 3H_2O$
Aunite or Alum stone	$K_2SO_4.\ Al_2(SO_4)_3\ .4Al(OH)_3$
Turquoise	$AlPO_4.\ Al(OH)_3.H_2O$
Beryl	$3BeO.Al_2O_3.\ 6SiO_2$

ELECTROCHEMICAL SERIES

1. The series of elements obtained by arranging them in an decreasing order of reduction potential is known as electrochemical seres. ($M^{+n} + ne^- \rightarrow M$)

Table – 1 standard electrode potential (reduction potentail) at 25ºC

S.No.	Metal ion	Potential in volts
1.	$Li^+ + e^- \rightarrow Li$	- 3.05
2.	$K^+ + e \rightarrow K$	- 2.93
3.	$Ca^{+2} + 2e \rightarrow Ca$	- 2.90
4.	$Na^+ + e \rightarrow Na$	- 2.71
5.	$Mg^{+2} + 2e \rightarrow Mg$	- 2.37
6.	$Al^{+3} + 3e \rightarrow Al$	- 1.66
7.	$Zn^{+2} + 2e \rightarrow Zn$	- 0.76
8.	$Cr^{+3} + 3e \rightarrow Cr$	- 0.74
9.	$Fe^{+2} + 2e \rightarrow Fe$	- 0.44
10.	$Ni^{+2} + 2e \rightarrow Ni$	- 0.23
11.	$Sn^{+2} + 2e \rightarrow Sn$	- 0.14
12.	$Pb^{+2} + 2e \rightarrow Pb$	- 0.13
13.	$Fe^{+3} + 3e \rightarrow Fe$	- 0.04
14.	$H^+ + e \rightarrow H$ or $\frac{1}{2} H_2$	- 0.00 (Reference)
15.	$Cu^{+2} + 2e \rightarrow Cu$	+ 0.34
16.	$Hg^{++} + 2e \rightarrow Hg$	+ 0.79
17.	$Ag^+ + e \rightarrow Ag$	+ 0.80
18.	$Pt^{+4} + 4e \rightarrow Pt$	+ 0.86
19.	$Au^+ + e \rightarrow Au$	+ 1.69

Some Important Alloy

1.	α - Iron	-	Fe (100%)
2.	Bronze	-	Cu(75–90%) + Sn (10 – 25%)
3.	Brass	-	Cu (60 – 80%) + Zn (20 – 40%)
4.	Aluminium Bronze	-	Cu(90%) + Al (10%)
5.	Gun metal	-	(Cu + Zn + Sn) (87 : 3 : 10)
6.	German Silver	-	Cu + Zn + Ni (2 : 1 : 1)
7.	Bell metal	-	Cu (80%) + Sn (20%)
8.	Monel Metal	-	Cu : Ni : (Fe + Mn) (30 : 67 : 3)
9.	Nichrome	-	(Ni + Cr + Fe) (24 : 26 : 28)
10.	Alnico	-	(Al, Ni, Co)
11.	Britania Metal	-	(Sn + Pb)
12.	Babbit metal	-	Sn + Pb + Cu
13.	Munz metal	-	Cu + Zn (60 – 62%) – (68 – 40%)
14.	Type metal	–	Pb + Sn + Sb
15.	Alloys of steel		
	[1] Vanadium steel		V (0.2 – 1%)
	[2] Chromium steel		Cr (2 — 4%)

	[3] Nickel Steel		Ni (3 – 5%)
	[4] Manganese steel Mn (10 – 18%)		Mn (10 – 18%)
	(e) Stainless steel		Cr (12 – 14%) & Ni (2 – 4%)
	(f) Tungston steel		W (10–20%)
	(g) Invar		Ni (36%)
16.	14 Carat Gold	-	54% Au + Ag (14 to 30%) + Cu (12–28%)
17.	24 Carat Gold	-	100% Au
18.	Genny Gold or coil of Gold	-	Au + Cu (11 : 1)
19.	Solder	-	Pb + Sn
20.	Delta metal	-	Cu + Zn + Fe
21.	Coin of Silver	-	Ag (92.5%) + Cu (7.5%)
22.	Coin of aluminium	-	Mg + Al
23	Coin of Steel	-	3.5% Ni in steel
24.	Magnellium	-	Mg (10%) + Al(90%)
25.	Duralumin	-	(Al + Mn + Cu)
26.	Y-alloy	-	Al(93%) + Cu(4%) + Ni(2%) + Mg (1%)
27	Dutch metal	-	Cu (80%) + Zn (20%)
28.	Artificial Gold	-	Cu(90%) + Al(10%)
29.	Constantan	-	Cu(60%) + Ni(40%)
30.	Rinman Green	-	CoZnO2

B. % of Carbon in different type of Iron

	Name	% of C
[1]	Wrought iron/Meleable	0.1 to 0.25
[2]	Steel	0.25 to 2.0
[3]	Pig Iron	2.3 to 4.6
[4]	Cast Iron	2.6 to 4.3

SUM IMPORTANT COMPOUNDS/ MINERALS/ MIXTURE & THERE FORMULA'S

1.	Epsom salt	-	$MgSO_4.7H_2O$
2.	Gypsom salt	-	$CaSO_4.2H_2O$
3.	Glober's salt	-	$Na_2SO_4.10H_2O$
4.	Lime water	-	$Ca(OH)_2$(slaked lime)
5.	Quick lime	-	CaO
6.	Washing soda	-	$Na_2CO_3.10H_2O$
7.	Crystal carbonate	-	$Na_2CO_3.10H_2O$
8.	Soda ash	-	Na_2CO_3
9.	Baking Soda	-	$NaHCO_3$
10.	Baking powder	-	$NaHCO_3$ Tartaric acid
11.	Plaster of pairs	-	$2CaSO_4.H_2O$ or $CaSO_4.1/2\ H_2O$
12.	Chile salt petre	-	$NaNO_3$
13.	Indian salt petre	-	KNO_3
14.	Brine or table salt or rock salt -		NaCl
15.	Potash ash or pearl ash	-	K_2CO_3
16.	Nitre or Indian salt petre or chemical refrigerator	-	KNO_3
17.	Norwegian salt petre	-	$Ca(NO_3)_2$

18.	Salt Cake	-	K_2SO_4
19.	Carnalite	-	$KCl, MgCl_2.6H_2O$
20.	Hypo	-	$Na_2S_2O_3, 5H_2O$
21.	Borax) or Tineal	-	$Na_2B_4O_7,10H_2O$
22.	Barytes or Heavy spar or Barium meal	-	$BaSO_4$
23.	Baryta	-	$Ba(OH)_2$
24.	Magnesia	-	MgO
25.	Microcosmic salt	-	$NaNH_4HPO_4.4H_2O$
26.	Nitrolim	-	$CaCN_2$
27.	Hydrolith	-	CaH_2
28.	Fusion mixture	-	$Na_2CO_3 + K_2CO_3$
29.	Gun powder	-	KNO_3
30.	Pink salt	-	$(NH_4)_2SnCl_6$
31.	Laughing gas	-	N_2O (Nitous oxide)
32.	Red Lead	-	Pb_3O_4
33.	Blue vitreol	-	$CuSO_4 . 5H_2O$
34.	Green vitreol	-	$FeSO_4.7H_2O$
35.	White vitreol	-	$ZnSO_4.7H_2O$
36.	Phiiosopher's wool	-	ZnO
37	Oil of Vitreol	–	H_2SO_4
38.	Mohr's salt (Ferrous ammonium sulphate)	–	$FeSO_4(NH_4)_2SO_4.6H_2O$
39	Lunar Caustic		$AgNO_3$
40	Calomel		Hg_2Cl_2
41	Corrosive sublimate		$HgCl_2$
42	Potash alum		$K_2SO_4.Al_2 (SO_4)_3 .24H_2O$
43	Chrom alum		$K_2SO_4.Cr_2(SO_4)_3.24H_2O$
44.	Ferric alum		$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$
45.	Chrome lemon		$PbCrO_4$
46	Pyrolusite	-	MnO_2
47	Cementite (Iron Carbide)		Fe_3C
48	Nessler's reagent		K_2HgI_4
49	Lead Sugar	-	$(CH_3COO)_2Pb$
50.	White lead	-	$Pb(OH)_2 2PbCO_3$
51.	Rock Phosphate	-	$Ca_3(PO_4)_2$
52.	Rochelle salt (Sodium potassium tarterate)		CH(OH)COONa I CH(OH)COOK
53	Flour spar		CaF_2
54.	Anhydrone	-	$Mg(ClO_4)_2$
55.	Asbestos	-	$CaMg_3(SiO_3)_4$
56.	Sorel's cement	-	$MgCl_2.5HgO. H_2O$
57.	Magnesia alba	-	$MgCO_3.Mg(OH)_3.3H_2O$

(used in tooth powders and tooth paste)

58 Lithopone - $BaSO_4 + ZnS$

59. Witherite - $BaSO_4$

60. Tough pitch Copper - 99.5% pure Cu

61. Oxone - Na_2O_2

2. [1] PARAMAGNETIC COMPLEX ION, HYBRIDIAZATION AND GEOMETRY

[1] $[Cr(H_2O)]^{+3}$ (d^2sp^3)	(Octahedral)
[2] $[Cr(CN)_6]^{-3}$ (d^2sp^3)	(Octahedral)
[3] $[CoF_6]^{-3}$ (sp^3d^2)	(Octahedral)
[4] $[Ni(H_2O)_6]^{+2}$ (sp^3d^2)	(Octahedral)
(5) $[NiCl_4]^{-2}$(sp^3)	(Tetrahedral)
(6) $[Cu(NH)_4]^{+2}$ (dsp^2)	(Tetrahedral) or $[Zn(NH_3)_4]^{+2}$
(7) $[CoF_6]^{-3}$ (sp^3d^2)	(Octahedral)

[2] DIAMAGNETIC COMPLEX AND HYBRIDISATION & GEOMETRY

[1] $[Ni(Co)_4]$ (sp^3)	(Tetrahedral)
[2] $[Ni(CN)_4]^{-2}$ (dsp^3)	(Square Planer) or $[Pt(NH_3)_4]^{+2}$
[3] $[Co(NH)_5]^{+3}$ (d^2sp^3)	(Octahedral)
[4] $[Co(H_2O_6)]^{+3}$ (d^2sp^3)	(Octahedral)
(5) $[Co(NO)_2]^{-3}$ (d^2sp^3)	(Octahedral)
(6) $[Co(CN)_6]^{-3}$ (d^2sp^3)	(Octhedral)
(7) $[Fe(CN)_6]^{-4}$ (d^2sp^3)	(Octahedral)