GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

EXTRACTION OF ZN, FE, CU, AL

❖ EXTRACTION OF SOME METALS

(A) EXTRACTION OF COPPER

Copper is mainly extracted from copper pyrites. After the concentration of its ore by froth flotation process, the ore is roasted in a current of air to remove arsenic, antimony and much of sulphur. The reactions occurring are

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2 \uparrow \text{ (major reaction)}$$

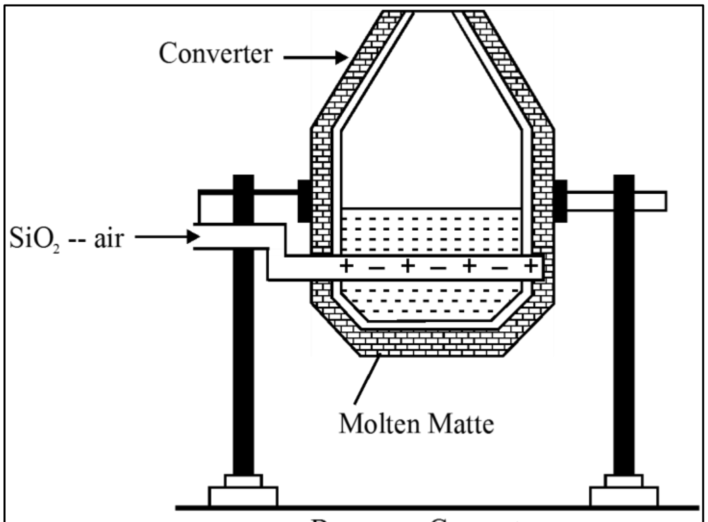
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \qquad \text{(minor reactions)}$$

The ore is then mixed with a little coke and sand and smelted in a water-jacketed blast furnace. The minor reactions that occurred during roasting continue here. Ferrous oxide combines with sand to form a fusible slag. Cuprous oxide formed combines with ferrous sulphide to give ferrous oxide and cuprous sulphide. This is because iron has more affinity for oxygen than copper.

$$FeO + SiO_2 \longrightarrow FeSiO_3 \;;\quad Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

Molten mass collected from the bottom of furnace contains largely cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte.



Bassemer Converter

The molten matte is finally transferred to Bessemer converter. A blast of sand and air is blown in the converter through tuyeres which are situated a little above the bottom. This causes removal of S and As oxides and ferrous oxide as slag. At the same time Cu_2S is oxidized mostly into Cu_2O and partly into CuO and $CuSO_4$. All these react with Cu_2S giving copper.

The reactions are

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

$$2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$$

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

$$CuSO_4 + Cu_2S \longrightarrow 3Cu + 2SO_2 \uparrow$$

$$Cu_2S + 2CuO \longrightarrow 4Cu + SO_2 \uparrow$$

Finally, copper may be refined electrolytically (electrolyte; copper sulphate: anode; impure copper and cathode; pure copper).

(B) EXTRACTION OF LEAD

Lead is mainly extracted from galena. After the concentration of the ore by froth flotation process, the ore is roasted in a reverberatory furnace for about six hours at a moderate temperature in a current of air. Part of galena is converted into lead oxide and lead sulphate. After this, the supply of air is stopped and small quantities of carbon, quicklime and cheap iron ore are added along with increase of temperature. At this stage, unreacted sulphide reacts with the lead oxide and sulphate giving metallic lead:

$$PbS + 2PbO \longrightarrow 3Pb + 2SO_2$$

$$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$$

The obtained lead contains impurities such as Cu, Ag, Bi, Sb and Sn. Silver is removed by Parke's process where molten zinc is added to molten impure lead. The former is immiscible with the latter. Silver is more soluble in molten zinc than in molten lead. Zinc-silver alloy solidifies earlier then molten lead and thus can be separated. After this, crude lead is refined electrolytically (Electrolyte; lead silicofluoride, $PbSiF_6$ and hydrofluosilicic acid, H_2SiF_6 with a little gelatin, anode, crude lead and cathode; pure lead).

(C) EXTRACTION OF IRON

FLOW SHEET FOR EXTRACTION OF IRON

↓

Concentration
By
Gravity process followed
by electromagnetic separation

↓

Calcination and Roasting

$$\text{Ore} + \text{air} \xrightarrow{Heat} \text{moisture}, CO_2, SO_2\ \ As_2O_3$$

FeO is oxidised to ferric oxide

Smelting in a blast furnace (ore+ coke+ limestone). The following Reactions occur.

$$Fe_2O_3 + 3CO \xrightarrow{400-700°C} \underset{\text{Spongy iron}}{2Fe} + 3CO_2$$

$$CaCO_3 \xrightarrow{1000°C} CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3\ (\text{Slag})$$

$$2CO \xrightarrow{Hot\ iron} CO_2 + C$$

$$SiO_2 + 2C \xrightarrow{1200°C} Si + 2CO$$

$$MnO_2 + 2C \rightarrow Mn + 2CO$$

$$P_4O_{10} + 10C \rightarrow 4P + 10CO$$

$$\text{Spongy iron} + C, Mn, Si, \text{etc.} \rightarrow \text{Impure iron}$$

$$C + O_2 \xrightarrow{1600°C} CO_2$$

$$CO_2 + C \xrightarrow{1500°C} 2CO$$

↓

Pig iron

↓Remelted and Cooled

Cast iron

(Fe = 93% ; C= 5% and impurities of Mn, P, Si, etc.= 2%)

Iron is extracted from its principal ore, hematite. After the preliminary washing, concentration and roasting, the ore is smelted in the presence of coke and limestone in a blast furnace.

Roasted ore (8 parts) with desulphurized coke (4 parts) and limestone pieces (1 part) is fed into the blast furnace from the top. (Preheated air is blown in through water - jacketed pipes called tuyeres fixed in the lower part of the furnace). There is a temperature gradient as we move from the bottom (temperature about 2000K) to the top (temperature about 500K) of the blast furnace.

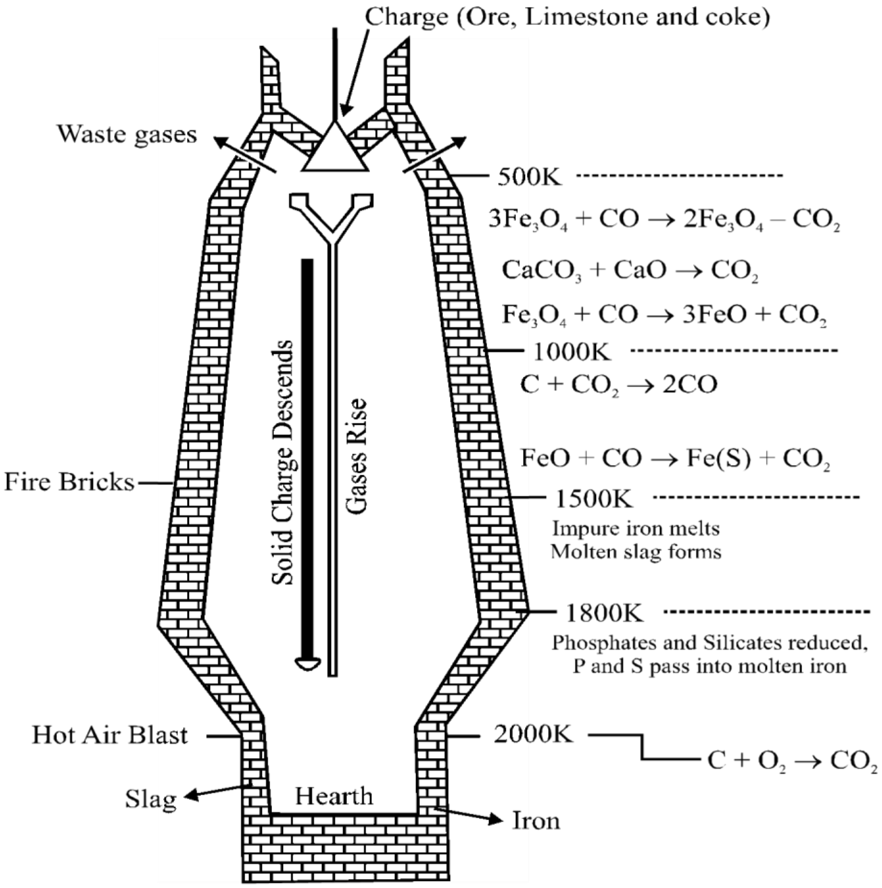
The blast furnace may be broadly divided into three main parts as described in the following.

(a) Zone of Fusion

The lower portion where coke burns and produced carbon dioxide and a lot of heating is known as zone of fusion:

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -406 \text{ kJ mol}^{-1}$$

Here the temperature is about 1775 K. A little above this, where temperature is above this, where temperature is about 1475 K – 1575 K, iron coming from above melts.



Beast Furnace

(b) Zone of Heat Absorption

The middle portion (temperature 1075 K – 1275 K), CO_2 rising up is reduced to CO with the absorption of heat:

$$CO_2 + C \longrightarrow 2CO \quad \Delta H = 163 \text{ kJ mol}^{-1}$$

In this portion, limestone coming from above is decomposed and the resultant lime (CaO), which acts as flux, combines with silica (present as impurity - gangue) to form calcium silicate (fusible slag):

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

(c) Zone of Reduction

The upper portion (675K – 975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up to furnace

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

The reduction is believed to take place in stages:

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

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron form oxidation. These two can be removed from different holes (fig.). Waste gases escaping at the top consists of about 30% CO, 10% CO_2 and the rest nitrogen.

Iron obtained from the blast furnace is known as pig iron.

Pig iron contains about 2–5% carbon as well as other impurities (usually Si, Mn, S and P). Pig iron is converted into cast iron by remelting in a vertical furnace heated by coke. Cast iron expands on solidification and is used for casting various articles. Wrought iron, which is the purest form of iron can be obtained by heating cast iron in a reverberatory furnace lined with iron oxide. Wrought iron contains about 0.2% carbon.

(D) MANUFACTURE OF STEEL

Different method is used: –

(a) Bessemer Process

This process is based on the fact that impurity of the pig iron is completely oxidised in presence of hot air blast.

This process involves the use of a large pear- shaped furnace (vessels) called Bessemer converter.

(b) BOP Method (Basic Oxygen Process)

The process is carried out in a steel vessel with a refractory lining (usually made of dolomite, $CaCO_3$, $MgCO_3$). Oxygen gas at about 10 atm pressure and a stream of powdered limestone are fed through a water-cooled lance and discharged above the molten pig iron.

$$2C + O_2 \longrightarrow 2CO$$

$$2FeO + Si \longrightarrow 2Fe + SiO_2$$

$$FeO + Mn \longrightarrow Fe + MnO$$

$$FeO + SiO_2 \longrightarrow FeO.SiO_2$$

$$MnO + SiO_2 \longrightarrow MnO.SiO_2 \text{ (slag)}$$

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$$

The properties of steel depend on its chemical composition but also on heat treatment. At high temperatures, iron and carbon in steel combine to form iron carbide, Fe_3C, called cementite :

$$3Fe\ (s) + C\ (s) \rightarrow Fe_3C(s)$$

The forward reaction is endothermic, so that the formation of cemetite is favoured at high temperatures. When steel containing cemetite is cooled slowly, the above equilibrium shifts to the left, and the carbon separates as small particles of graphite, which give the steel a gray colour. If the steel is cooled rapidly, equilibrium is not attained and the carbon remains large in the form of cementite, Fe_3C. Steel containing cementite is light in colour, and is harder and more brittle than that containing graphite.

(c) Heat Treatment of Steel

Quenching or Hardening

Steel is heated to red hot temp. and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.

Annealing

The steel is heated to red hot temp. and then cooled slowly.

It makes steel soft.

Tempering

If quenched steel is heated to temp. between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

Surface Treatment of Steel

(i) Nitriding - Process of heating steel at 1000 K in an atmosphere of NH_3.

This gives hard coating of iron nitride on the surface.

(ii) Case hardening - Process of giving a thin coating of hardend steel, by heating steel in contact with charcoal followed quenching in oil.

It is used for axles of railway wagons.

(d) Types of Iron

Cast Iron or Pig Iron

It is most impure form of Iron and contains the higest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig contain 2.5 to 5%.

Wrought Iron (Fibrous Iron) or Malleable Iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 5% of other impurities.

Steel

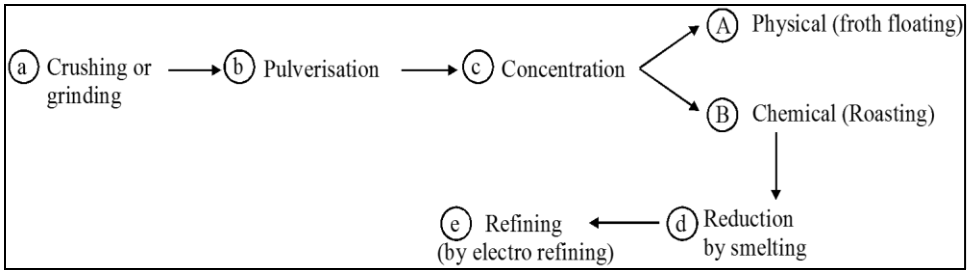
It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon.

Thus, all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Order of M.P. WI > Steel > CI or PI

(E) EXTRACTION OF ZINC (Zn)

ORE ⟶ Zinc blende or Black jack (ZnS)



USES

(a) Zn–Cu couple, Zn- Hg, zinc dust etc. are used as reducing agent in organic reactions.

(b) large amounts of zinc are used for galvanizing iron. Zinc is deposited on the surface of iron articles. This process is called galvanization.

(c) $ZnSO_4 .7H_2O$ (White vitrol) issued as eye lotion.

(F) EXTRACTION OF SILVER AND GOLD

Cyanide Process: Silver and gold are extracted by the cyanide process (Mac Arthur - Forrest process). After the preliminary crushing and concentration by forth floatation process, the ore (crushed auriferous rocks in the case of gold) is leached with dilute (0.4 - 7%) solution of sodium cyanide made alkaline by adding lime kept agitated by a current of air. Silver (or gold) pass into solution as argent cyanide (or aurocyanide) :

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

The air blown in remove Na_2S and $Na_2S_2O_3$ and Na_2SO_4 causing the above reaction to proceed to completion.

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

$$Na_2S_2O_3 + 2NaOH + 2O_2 \longrightarrow 2Na_2SO_4 + H_2O$$

$$4Au + 8NaCN + 2H_2O \leftrightarrow 4Na[Au(CN)_2] + 4NaOH$$

The solution obtained above is filtered and treated with scrap iron or zinc when silver (or gold) get precipitated:

$$2Ag(CN)_2^- + Zn \longrightarrow Zn(CN)^{2-}{}_4 + 2Ag$$

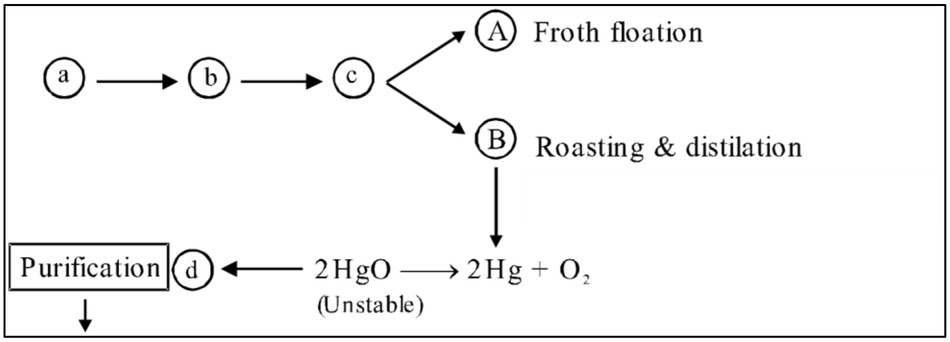
$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au$$

The obtained silver is purified electrolytically (electrolyte: silver nitrate solution containing 1% nitric acid, anode: impure silver, cathode: pure silver). The impurities like zinc and copper pass into the solution while gold falls down as anode mud.

Gold thus obtained is contaminated by zinc which is dissolved out by sulphuric acid. The dried residue of gold is then fused under borax (flux) in graphite crucible and the melted down gold (bullion) which invariably contain silver, is set for refining.

(G) EXTRACTION OF MERCURY (HYDRAGYRUM) (Hg)

Short Chart of Hg (Hydragyrum) by HgS (Cinnabar or Vermilon)



(a) Pb & Zn remove as oxide.

(b) Basic metal remove as nitrate in HNO_3

(c) Final purification done by vacuum distillation.

PROPERTIES

(a) It vigorously combines with Cl_2 slowly with Br_2 and I_2.

(b) Hot conc. H_2SO_4, dil. & conc. HNO_3 dissolve it.

(c) Mercury is acted upon by HI on account of the formation of a complex ion$(HgI_4)^{2-}$

$$Hg + 2HI \rightarrow HgI_2 + H_2$$

$$HgI_2 + 2HI \rightarrow H_2HgI_4$$

(d) Hg dissolves many metals and the combinations are called amalgams. Au, Ag, Sn, Pb,Mg, Cu, Na, K etc. rubbed with mercury form amalgams. Co, Fe and Ni do not form amalgam directly.

USES

Mercury is used :

(a) In thermometers, barometers and other physical apparatus.

(b) In the extraction of Ag and Au. In amalganation process.

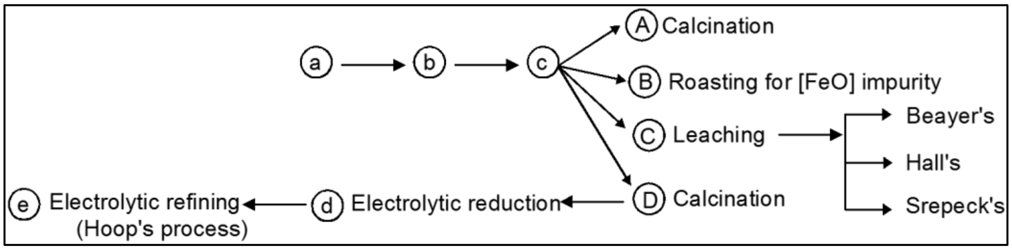
(c) In the form of amalgams as reducing agents.

(d) In mercury vapour lamps.

(e) In manufacture of vermilion (HgS).

(H) EXTRACTION OF ALUMINIUM

Short chart of Al from $Al_2O_3.2H_2O$ (Bauxite)



Bauxite

↓

Concentration of Bauxite ore

(a) Baeyer's Process: (Used for red bauxite in which main impurity is iron oxide)

Bauxite ore $\xrightarrow{Roasted}$ as to convert FeO into Fe_2O_3

Roasted ore + NaOH $\xrightarrow[8\text{ atm}]{150^\circ C}$ $NaAlO_2$ $\xrightarrow{Hydroly\ sis}$ $Al(OH)_3 + NaOH$

solution in presence ppt.

of little $Al(OH)_3$

(b) Hall's Process: (Red bauxite)

Bauxite ore + Na_2CO_3 $\xrightarrow{Fused}$ $NaAlO_2$

↓ extracted with water

Solution

↓ warmed 50° – 60° C

CO_2 is circulated

↓

$Al(OH)_3 + Na_2CO_3$

(c) Serpeck's Process: (Used for white bauxite in which main impurity is silica)

Bauxite ore + coke 1800°C AlN $\xrightarrow{H_2O}$ $Al(OH)_3 + NH_3$

+ppt. (Nitrogen) N_2 $C + SiO_2$ (gangue) $CO_2 +$ Si

↓

CALCINATION

$$Al(OH)_3 \xrightarrow{1500°C} Al_2O_3$$

↓

Electrolytic Reduction

Electrolyte Al_2O_3 dissolved in Na_3AlF_6 and CaF_2

Cathode–Carbon lining

Anode – Graphite rods

$$Al_2O_3 \xrightarrow[950°C]{Electrolysis} Al + O_2$$

↓ 99.8% pure

Electrolytic Refining

(Hoop's process)

Pure Al (99.98 % pure)

IMPORTANT POINTS

(a) Useful gas NH_3 is evolved in the leaching of bauxite by Serpeck's process.

(b) In the electrolytic reduction of Al_2O_3 cryolite (Na_3AlF_6) is added along with CaF_2 (fluorspar) to–

- decrease m.p. of Al_2O_3
- decrease viscosity of electrolyte (CaF_2 is used)
- increase conductivity

(c) In the electrolytic reduction graphite anode get corrode or finished due to reaction with O_2 liberates at anode, hence it had to be changed periodically.

(d) In the electrolytic refining (4th step) no electrodes are used. In the Hoop's process molten pure Al is used as cathode and molten impure Al is used as anode.

(e) In the Hoop's process carbon dust is sprayed over molten Al to

- avoid heat lose
- minimize metallic lusture (glaze) which is harmful for the eyes.

(I) EXTRACTION OF MAGNESIUM

Magnesium is commonly obtained by the electrolysis of fused magnesium chloride containing a little (25%) sodium chloride and sodium fluoride at 700^0C in an air–tight iron pot which itself serves as the cathode, the anode being a graphite rod which dips into the electrolyte. The anode is surrounded by a perforated porcelain tube for the exit of chlorine. The electrolysis is carried out in the atmosphere of coal gas so as to prevent the attack of atmospheric oxygen and nitrogen on magnesium. Molten magnesium being lighter then the electrolyte, it floats over the fused electrolyte and is withdrawn

In Dow process, magnesium is recovered from seawater as magnesium chloride which is then electrolyzed using cell described above.

Dow's Sea Water Process: Sea water contains 0.13% Mg ions

Mg^{2+}(seawater) + $Ca(OH)_2$(from oyster shells) → $Mg(OH)_2 + CaCl_2$ $MgCl_2.2H_2O$

$MgCl_2.2H_2O$ $MgCl_2.1.5H_2O$ $MgCl_2$

Dow's Natural Brine Process

$MgCO_3.CaCO_3$ $MgO.CaO$ $CaCl_2$ (aq)+ $MgCl_2$(aq) $MgCl_2$(aq) + $CaCO_3$
(dolomite) (calcined dolomite)

The reaction is :

$$CaCl_2.MgCl_2(aq) + MgO.CaO + 2CO_2 \longrightarrow MgCl_2(aq) + 2CaCO_3 \downarrow$$

Electrolysis:

Anhydrous carnallite may also be employed as the starting material of magnesium chloride. The cathode may be a layer of molten lead on the floor of the cell and anode may be graphite rods which are suspended above the molten lead. Magnesium liberated at the cathode dissolves in molten lead. The alloy of lead–magnesium is subjected to electrolysis to obtain pure magnesium (electrolyte: fused carnallite, anode : lead–magnesium alloy and cathode–steel rods.)

Some Important Compound and their formulae

Lunar caustic (Highly photo sensensitive)	$AgNO_3$
Monozite	ThO_2
Calomal	Hg_2Cl_2
Iℓimanite	TiO_2
Corrosive sublimate	$HgCl_2$

(does not give chromyl chloride test)

Type metal	Pb+Sn+Sb
Constantan	Cu(60%) +Ni (40%)
Litharge	PbO
Red Lead (OR) Sindhur	Pb_3O_4
Butter of tin	$SnCl_4 .5H_2O$

Spelter (Impure Zn during extraction of Zn) Crude zinc metal called spelter which contain nonfusible impurities and the impurities of Pb, Fe, Cd.

Green vitrol	$FeSO_4 . 7H_2O$
Blue vitrol	$CuSO_4 . 5H_2O$
White vitrol	$ZnSO_4 .7H_2O$

Lithopone	$BaSO_4$+ ZnS
Nessler Reagent in basic medium	K_2HgI_4
Mohr salt (ferrous Ammonium sulphate)	$FeSO_4 \cdot (NH_3)_2SO_4 \cdot 6H_2O$
Ignition mixture	Mg powder + BaO_2
Fusion mixture	Na_2CO_3+ K_2CO_3
Freezing mixture	NaCl is used with ice
Electron	Mg (95%) + Zn (5%) used in aircraft