CHAPTER 18 METALLURGICAL

18.1 INTRODUCTION

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called ores. An ore is usually contaminated with earthy or undesired materials known as gangue. Hence, all minerals are not ores but all ores are minerals.

Oxides and hydroxides: Fe, Cu, Zn, Ni, Bi, Cd and Sn; Carbonates: Fe, Cu, Zn, Pb, Ca, Mn and Mg. Sulphates: Mg, Ba, Ca and Pb Silicates: Cu, Zn Ni, Al, Li, Na, K and Be; Nitrates: Na and K Phosphates: Li, Na, K, Ca, Fe and Mn;

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Nitrate ores are rare because all nitrates are water soluble and at higher temperature they decomposes into oxides of their metal.

Important Ores of Some Metals 18.1.1

- 1. Iron: In the combined state iron occurs in the following minerals.
 - (i) Haematite (Fe_2O_3) : main ore
 - (ii) Magnetite (Fe_3O_4)
 - (iii) Limonite $(3Fe_2O_3 \cdot 3H_2O)$
 - (iv) Siderite (FeCO₂).
- 2. Tin: Cassiterite or tin stone (SnO₂): main ore
- 3. Copper: Occurs in the native state as well as in the compound form. The natural ores of copper are
 - (i) Copper pyrites (CuFeS₂): main ore
 - Malachite (Cu(OH), CuCO₃) (green colour) (ii)
 - Cuprite or ruby copper (Cu₂O) (iii)
 - Azurite(CuOH), 2CuCO,) (iv)
 - (v) Copper glance (Cu₂S)
- 4. Lead
 - (i) Galena (PbS): main ore

(ii) Cerrusite (PbCO₂)

(iii) Anglesite (PbSO₄)

(iv) Wulfenite (PbMnO₄)

(v) Stozite (PbWO)

5. Magnesium:

- (i) Dolomite $(MgCO_3 \cdot CaCO_3)$: main ore
- (iii) Asbestor: (CaSiO₃·3MgSiO₃)
- (vi) Schonite (MgSO₄· K_2 SO₄· $6H_2$ O)
- (ii) Carnallite (MgCl₂·KCl·6H₂O)
- (iii) Magnesite ($MgCO_3$).

(iv) Cryolite (Na_3AlF_4)

(ii) Braunite (Mn_2O_3)

(ii)

(vii) Epsom salt (MgSO₄·7H₂O)

Diaspore $(Al_2O_2 \cdot H_2O)$

6. Aluminium: Aluminium is the third most abundant element of earth's crust.

- (i) Corundum (Al_2O_3) : main Ore
- (iii) Bauxite $(Al_2O_3 \cdot 2H_2O)$
- (vi) Alumstone $(K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al(OH)_3)$

7. Silver: In the native form it is associated with copper and gold. The main ores of silver are

- (i) Argentite or silver glance (Ag₂S): **main ore**
- (ii) Horn silver (AgCl)
- (iii) Proustite or ruby silver $(3Ag_2S \cdot As_2S_3)$
- (iv) Pyrargyrite $(3Ag_2S \cdot Sb_2S_3)$ i.e., Ag_3SbS_3 .
- **8. Manganese:** (i) Pyrolusite, (MnO_2)

9. Zinc: (i) Zinc blende (ZnS) (ii) Calamine (ZnCO₃) (iii) Zincite (ZnO) Oxygen is the most abundant element in the earth's crust by weight. Aluminium is the most abundant metal in the earth's crust. Most abundant element in the atmosphere is nitrogen.

18.1.2 Other Important Ores

- $\Box \quad Fluorspar (CaF_2) \qquad \Box \quad Gypsum (CaSO_4 \cdot 2H_2O)$
- **D** Pitch blende (U_3O_8)
- Cinnabar (HgS)
- $\square \quad \text{Borax} (\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O})$
- $\Box \quad \text{Chile salt peter (NaNO_3)}$
- □ Indian salt peter (KNO₃) □ Rutile (TiO₂)

18.2 METALLURGICAL OPERATION

Flow sheet for the general metallurgical operation is given below. In the flow sheet, the functions of process are given on the right side, whereas the methods employed are denoted on the left.

- (A) **Crushing and grinding:** The ore is first crushed by jaw crushers and ground in various size reduction equipments like ball mill, jaw crusher, etc.
- (B) Concentration or dressing of the ore: The process of removal of the unwanted material (gangue) from the ore is called concentration or dressing or benefaction of the ore. The important methods for concentration are listed hereunder.
 - (i) Hydraulic washing or gravity separation or levigation method: The method is based on the difference in specific gravities of the ore and gangue particles. It is also known as gravity separation method. The powdered ore is washed with an upward stream of running water, where the lighter gangue particles are washed away while the heavier ore particles are left behind, e.g., ores [like tinstone (SnO₂), haematite (Fe₂O₃), chromite (FeO·Cr₂O₃), etc.] are concentrated by this method.

Gangue or matrix: The non-metallic impurities such as mica, earth particles, etc. associated with crude ore are known as gangue or matrix.



(ii) **Magnetic separation:** The method is based on magnetic and non-magnetic properties of the two components of the ore. This method has limited application. The ground ore is carried on a travelling band which passes over a magnetic roller. The ore leaves the band and falls from it. The particles attracted by the magnetic field form a separate pile. This method is useful for separating tin ore particles from cassiterite (SnO_2) . The process may also be employed for separating other transition metal ores such as magnetite (Fe_3O_4) , chromite $(FeO\cdot Cr_2O_3)$ and pyrolusite (MnO_2) from unwanted gangue.

The method is used for strongly ferromagnetic ores of Fe, Sn, etc. Wolframite (FeWO₄) is a magnetic ore that can be separated from the non-magnetic ore cassiterite (SnO₂).



(iii) Froth floatation method: This is a very useful technique especially for separating sulphide ores of zinc, copper and lead from the gangue. A suspension of the finally powdered ore is made with water. Suspension is mixed with 3.5 per cent by weight of eucalyptus oil (or some other cheap oil) and the mixture is stirred by compressed air. Froth is generated at surface. Sulphide particles in ores are preferentially wetted by this froth and rise to the surface. They are skimmed off by a skimmer. Gangue is preferentially wetted by water and sinks to bottom.

Reagents used in froth floatation process

- (a) Froathers: Which create froth, e.g., palm oil.
- (b) **Collectors:** The surface of collectors adsorb small ore particles and these collector particles come with froth air bubbles. E.g., ethyl xanthate or potassium ethyl xanthate.
- (c) Activators: Simple inorganic compounds which enhance the effect of collectors, e.g., Na,S, CuSO₄, etc.



- (d) Depressants: Depressants are used to prevent certain type of particles from forming the froth with the bubbles. E.g., sodium cyanide can be used as a depressant in the separation of zinc sulphide ore (ZnS) and lead sulphide ore (PbS). NaCN acts as a depressant for ZnS but does not prevent PbS from the formation of froth, e.g., NaCN, Na₂CO₃, KCN, etc. NaCN forms a layer of zinc complex, Na₂Zn(CN)₄ on the surface of ZnS and thereby prevents it from the formation of froth.
- (iv) Leaching: This method is useful in cases where ore is soluble in a suitable solvent, but impurities are insoluble. E.g., in Baeyer's process pure aluminium oxide is obtained from the bauxite ore by treating the powdered ore with a concentrated solution of sodium hydroxide where Al_2O_3 dissolves leaving behind the impurities.

 $Al_2O_{3(s)} + 2OH_{(aq)}^- + 3H_2O \rightarrow 2Al(OH)_{4(aq)}^-$

The solution of sodium aluminate is filtered and cooled and its pH is adjusted downward by dilution and/or neutralization with CO_2 where aluminium hydroxide is precipitated; seeding with a little freshly precipitated aluminium hydroxide quickens the process.

 $Al(OH)_{4}^{-}(aq) \xrightarrow{Dilution} Al(OH)_{3(s)} + OH_{(aq)}^{-}$

The precipitate of $Al(OH)_3$ is filtered, dried and finally heated to about 1473 K to obtain pure Al_2O_3 .

 $2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$

In the metallurgy of silver and that of gold, the respective metal/ore leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement.

 $4M_{(s)} + 8CN_{(aq)}^{-} + 2H_{2}O_{(aq)} + O_{2(g)} \rightarrow 4[M(CN)_{2}]_{(aq)}^{-} + 4OH_{(aq)}^{-}$ $2[M(CN)_{2}]_{(aq)}^{-} + Zn_{(s)} \rightarrow [Zn(CN)_{4}]_{(aq)}^{2-} + 2M_{(s)}$

(C) Extraction of the crude metal from the concentrated ore

The concentrated ore must be converted into a form which is suitable for reduction to the metal. If the ore is a hydroxide (hydrated oxide), carbonate or sulphide it is subjected to calcination or roasting/melting and thereby converted to the oxide form, for thermodynamic reasons it is easier to reduce an oxide than the sulphide.

(i) **Calcination:** When the ore is heated below its melting point in limited supply of air, mainly decomposition reactions occur. This process is known as calcination. Calcination is highly endothermic. A reverberatory furnace is usually employed for carrying out calcination.

During calcination:

- (a) All the volatile impurities are lost.
- (b) Water of crystallizations is lost. E.g., $Al_2O_3 \cdot 2H_2O \rightarrow Al_2O_3 + 2H_2O_{(g)}$

Calcination reactions are: $2Al(OH)_3 \xrightarrow{\Lambda} Al_2O_3 + 3H_2O_3$

 $Al_2O_3 \cdot 2H_2O \xrightarrow{\Lambda} Al_2O_3 + 2H_2O$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_3$$

- (ii) Roasting: Roasting is done at a temperature slightly higher than that of calcination in excess of air. The ore does not melt during roasting. All the combustible organic matter burns away and the ore becomes more porous. Exothermic reactions supply much of the heat and much lesser energy is required in this case. In the roasting process, ore is converted into its oxide or sulphate. The process of roasting is generally carried out in a reverberatory furnace or blast furnace.
 - e.g., $2 \text{ZnS} + 3\text{O}_2 \rightarrow 2 \text{ZnO} + 2\text{SO}_2$

$$\begin{array}{l} 2 \ \mathrm{PbS} + \mathrm{3O_2} \rightarrow 2 \ \mathrm{PbO} + \mathrm{2SO_2} \\ \mathrm{PbS} + \mathrm{2O_2} \rightarrow \mathrm{PbSO_4} \\ \mathrm{2Cu_2S} + \mathrm{3O_2} \rightarrow 2 \ \mathrm{Cu_2O} + \mathrm{2SO_2} \end{array}$$

In chloridizing roasting, the ore is changed into metal chloride by heating with common salts in presence of air.

 $\text{TiC} + 4\text{Cl}_2 \rightarrow \text{TiCl}_4 + \text{CCl}_4$ $\text{Ag}_2\text{S} + 2\text{NaCl} \rightarrow 2\text{ AgCl} + \text{Na}_2\text{S}$

Note:

The free energies of formation (ΔG_i°) of most sulphide ore are greater than those for CS₂ and H₂S. CS₂ is, in fact, an endothermic compound. So neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Moreover, the roasting of a sulphide to the oxide is quite advantageous thermodynamically. Hence, the common practice is to roast sulphide ore to the oxide prior to reduction.

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(iii) Smelting: The process of extraction of metal in fused (molten) state is called smelting. This process is carried out in blast furnace. During melting, the ore is heated with suitable reducing agent in order to obtain the metal. During this process, some infusible impurities are also removed from molten metal by adding suitable substance known as flux. Even after concentration, ore may contain some infusible impurities, which may be acidic, i.e., non-metallic oxides like SiO₂, P₂O₅, etc. or basic, i.e., metallic

oxides like CaO, FeO, etc. Impurity + Flux \rightarrow Slag (fusible mass, which floats over molten metal)

Slag is a fusible mass and has low m.pt. It is lighter than metal and is immiscible with molten metal; hence, it floats over the metal. The layer of slag over molten metal prevents the metal from oxidation.

(a) Acidic flux: They are used to remove basic impurities like CaO, MgO, FeO, etc. They are acidic in nature, i.e., oxides of non-metals, e.g., SiO₂, P₂O₃, B₂O₃, etc.

 $\begin{array}{cccc} {\rm SiO}_2 & + & {\rm CaO} & \rightarrow {\rm CaSiO}_3 \\ {\rm Acidic \ flux} & & {\rm Basic \ impurity} & {\rm Slag} \end{array}$

(b) **Basic flux:** Basic flux removes acidic impurities like SiO₂, P₂O₅, etc. and is basic in nature. e.g., CaO, (obtained from limestone), MgO (obtained from magnesite MgCO₃), etc.

SiO ₂	+	CaCO ₃	$\rightarrow CaSiO_3 + CO_2$
Acidic flux		Basic impurity	Slag

Some important reduction process are described below:

18.3 REDUCTION CONVERSION OF ORE TO METAL

The ore, obtained after calcination or roasting, is reduced to metal and choice of reducing agent depends upon the nature of the ore. Some common reducing agents are listed hereunder:

(a) Reduction by Carbon and Carbon Monoxide

- (i) Due to cheapness and high availability, carbon is widely used as a reducing agent. The process is known as carbon reduction process.
- (ii) The metals which are less electropositive and do not form carbides with carbon are reduced by this method, e.g., oxides of Pb, Fe, Zn, Sn, etc.
- (iii) For reduction, the ore is strongly heated with coke or coal in blast furnace, where metal is obtained in the form of vapours, which are condensed (Zn) or in molten state (Sn, Fe, etc.) e.g.,

$$ZnO + C \xrightarrow{\Delta} Zn + CO; NiO + C \xrightarrow{\Delta} Ni + CO; Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$$

 $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$; (Devil's process)

- (iv) Some disadvantages of carbon reduction process are that some time metallic oxide may form carbide instead of the metal, e.g., $CaO + 3C \rightarrow CaC_2 + CO$. In some cases, reversible reaction may take place and so during the cooling, formation of oxide may take place, e.g., $MgO + C \Rightarrow Mg + CO$, thus carbon is not fit for reducing CaO and MgO.
- (v) Carbon monoxide also act as a reducing agent. e.g.,

 $\begin{array}{ll} PbO + CO \rightarrow Pb + CO_2; & FeO + CO \rightarrow Fe + CO_2; \\ Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2; & Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \end{array}$

Note:

- (i) Below 710°C, CO is a better reducing agent than carbon and the reverse is true at temperature higher than 710°C. It can explained on the basis of Ellingham diagrams given in the thermodynamics of metallurgy.
- (ii) Carbon is a good reducing agent for oxides but not for sulphides.

(b) Reduction by Metals:

- (i) Highly electropositive metals like Na, K, Li, Al, etc. are used to reduce the less electropositive metals like Cr, Cu, Mn, etc.
- (ii) Reduction by powdered aluminium is known as Gold-Schmidt aluminothermite process. This process is employed in cases where metals have very high m.pt. and are to be extracted from their oxides. In this process thermite (mixture of ore and powdered aluminium) is taken in a steel crucible. The reaction is started by using ignition mixture (Mg powder and barium peroxide). It is called thermite process because large amount of heat is released during the reduction, which fuses both ore and metal. E.g., reduction of Cr_2O_3 by Al powder takes place as follows:

 $Mg + BaO_2 \rightarrow BaO + MgO + Heat$

 $Cr_2O_3 + 2Al \xrightarrow{Heat} 2Cr_{(1)} + Al_2O_3 + Heat (112 \text{ kcal})$ Similarly, $3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3$

(c) Reduction by H₂ or water gas (CO + H₂)

(i) The oxides of metals, which are less electropositive than hydrogen (e.g., CuO, FeO, Ag₂O, etc.) may be reduced by this method. E.g.,

$CuO + H_2 \rightarrow Cu + H_2O$	$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$
$Ag_2O + H_2 \rightarrow 2Ag + H_2O$	$Cr_2O_3 + 3H_2 \rightarrow 2Cr + 3H_2O$
$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$	$2NiO + CO + H_2 \rightarrow 2Ni + CO_2 + H_2O$

- (ii) Water formed during the reaction escapes out in the form of vapours.
- (d) **Self-reduced or auto reduction:** Oxides of unreactive metals (like those of Hg, Pb, Cu, etc.) are reduced by air/anion of ore. Here, no external reducing agent is added. E.g.,
 - (i) Extraction of Hg from cinnabar: $2HgS + 3O_2 \rightarrow 2HgO + 2SO_3$; $2HgO + HgS \rightarrow 3Hg + SO_2$
 - (ii) Extraction of Cu from copper glance: $2Cu_2S + 3O_2 \rightarrow 3Cu_2O + 2SO_2$; $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$
 - (iii) Extraction of Pb from galena: $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$; $2PbO + PbS \rightarrow 3Pb + SO_2$

(e) Hydrometallurgy or displacement method

- (i) This method is based on the fact that a more reactive metal displaces less reactive metal from its salt solution.
- (ii) In this method, ore is converted into soluble form where more reactive metal is added in it. E.g.,
 - (a) Extraction of copper from malachite: $CuCO_3 \cdot Cu(OH)_2 \rightarrow 2CuO + H_2O + CO_2$ $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O; CuSO_4 + Zn \rightarrow ZnSO_4 + Cu \downarrow$
 - (b) Cyanidation process for Ag and Au: $Ag_2S + 4NaCN = 2Na[Ag(CN)_2] + Na_2S$ $Na_2S + 2O_2 \rightarrow Na_2SO_4$; $2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$
- (f) **Amalgamation process:** The process is used for extraction of noble metals like Pt, Au, Ag, etc. Finely powdered ore is treated with Hg to form amalgam. Amalgam, on distillation, is decomposed to the metal and Hg.

 $Ore + Hg \rightarrow Amalgam \xrightarrow{Distillation} Metal + Hg vapours$

- (g) Electrolytic reduction: It is the most commonly used method of reduction. The ores of highly electropositive metals like alkali metals and alkaline earth metals cannot be reduced by common reducing agents like H₂, C, etc., because of formation of carbides. For electrolytic reduction, oxide, hydroxide or halide (as suitable) ore is fused. If melting point is quite high, some substances are added to lower the fusion temperature. The quantitative aspects of electrolytic reduction are based on Faraday's laws of electrolysis. The cell used for electrolysis is known as electrolytic cell and its functioning may be explained as given below.

Let an ore AB (containing A^{n+} cation of metal and B^{n-} anion) is subjected to electrolytic reduction. $AB_{(1)} \rightarrow A^{n+} + B^{n-} \qquad A^{n+} + ne^- \rightarrow A_{(1)}$ (at cathode) $B^{n-} \rightarrow B + ne^-$ (at anode) The set of the set

The nature of electrode, EMF applied, etc. depends upon the nature of the metal.

18.4 ELLINGHAM DIAGRAM

During combination reactions, the entropy of system decreases. Therefore ΔS is negative for combination reaction. Gibbs free energy change, $\Delta G = \Delta H = T\Delta S$

 $M + \frac{1}{2}O_2 \rightarrow MO, \Delta H = -ve$ then ΔG will be less negative for this type of reaction if temperature is

increased as T Δ S becomes more negative. After a certain temperature, reaction will become non-spontaneous as the value of Δ G will become positive.

When activity of all reacting substances is unity, then $\Delta G = \Delta G^{\circ}$. For one mole common reactant (like oxygen, halogen, sulphur, etc.) value of ΔG° may be plotted against temperature. These ΔG° vs T curves are known as Ellingham diagrams.



18.4.1 Important Features of Ellingham Diagrams

- (i) A typical Ellingham diagram follows a straight line unless there is large entropy change due to melting or vapourization.
- (ii) All the plots slope upwards because ΔG° becomes more positive when temperature increases.
- (iii) At a certain temperature $\Delta G^{\circ} = 0$ and above this temperature, it is positive. The metal oxide (or other products like sulphide or halide) formation is spontaneous below this temperature. Theoretically, all oxide are thermally unstable provided that this temperature can be attained.

- (iv) A metal can reduce the oxide of metal placed above in the diagram, due to more negative free energy, e.g., Al can reduce Cr but not Mg or Ca.
- (v) Reducing behaviour of carbon : There may be three types of reactions:



For reaction (i), the volume of CO_2 formed is almost equal to volume of O_2 consumed. So, ΔS does not change significantly and Ellingham plot is almost horizontal.

Temperature °C

For reaction (ii), plot is downward and unlike other reactions in this reaction ΔG° value becomes more negative as temperature is increased. It is due to positive value of ΔS because here two volumes of CO are produced for one volume of O, consumed, thus ΔS is positive.

For reactions (iii), again ΔS is negative because 3 moles of gases react to form two moles gas and so ΔG° becomes more positive with rise in temperature.

The plots for three reactions cross at 710°C and it shows that formation of CO_2 from CO is more favoured below 710°C while at higher temperatures CO is formed preferably. Formation of CO_2 from carbon is not much affected by temperature.

Due to downward slope theoretically C will reduce any metal oxide provided that temperature is sufficiently high. However, it is not attempted due to possibility of formation of carbide at high temperatures and maintenance of such high temperature is not economically profitable. Below 710°C, CO is a better reducing agent than carbon because of more negative value of ΔG° of the reaction, $2CO + O_2 \rightarrow 2CO_2$, upto this temperature.

18.5 REFINING OR PURIFICATION OF METAL

The metals extracted by any of the above operations are in their crude form. The crude form is usually contaminated with impurities of following nature.

- (a) Impurities of other metals obtained by the simultaneous reduction of their respective oxides present in the ore as impurities.
- (b) Impurities of non-metals like silicon or phosphorous formed by reduction in the furnace.
- (c) Impurities of unreduced oxides and sulphides of the metals.
- (d) Impurities of residual slag, flux, etc. introduced during treatment in the furnace. To remove these impurities, the crude metal is subjected to the process of purification or refining. Refining of the crude metals may be done by the following methods depending upon the nature of the metal and impurities.

18.5.1 Electrolytic Refining

In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of same pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud or anode sludge.

18.5.2 Liquation Process

The refining process for crude metal based on the difference in fusibility of metal and impurities is named as liquation process. Zn–Pb mixture is separated by heating the crude Zn just above the melting point of Zn, whereas Pb remains as non fusible mass. The molten mass is allowed to flow on an inclined plane, whereas non-fusible mass is left behind.

18.5.3 Distillation Method

Volatile metals (Hg, Zn and Cd) are easily purified by distillation. The impure metal is heated in a retort and vapours of volatile metals are collected and condensed in a receivers leaving behind non-volatile impurities in a retort.

18.5.4 Heating of Crude form with Ores

Fe and Sb ores are heated with crude form which removes the contaminated reducing agents (S and C) with it and pure metal is obtained.

18.5.5 Oxidation Process

Impurities in crude form having more affinity for O_2 than the metal itself are oxidized in suitable furnaces. The oxides formed at the surface are skimmed off. The various oxidation processes used for different metals involve poling, puddling, bessemerization and cupellation.

- (a) **Poling:** The molten impure metal (Cu) containing oxides as impurity is stirred with green poles of wood which releases hydrocarbon gases. These hydrocarbon gases reduce oxide to metal.
- (b) **Puddling:** It involves the preparation of nearly pure wrought iron from cast iron that contains a high percentage of carbon. The cast iron is heated with hematite (Fe₂O₃), the oxygen of which oxidizes the carbon.
- (c) **Bessemerization:** A process for making steel from cast iron, named after its discoverer H. Bessemer. The impure molten metal is heated in a Bessemer converter (a large, egg-shaped vessel with holes below) and air is blown up to oxidize the impurities. Now the required amount of spiegel is added to introduce correct amount of carbon for the type of steel required.
- (d) Cupellation: The separation of silver, gold and other noble metals from impurities that are oxidized by hot air. The impure metal is placed in a cupel, a flat dish made of porous refractory material and a blast of hot air is directed upon it in a special furnace. The impurities are oxidized by air and are partly swept away by the blast and partly absorbed by cupel. This method is also based on different affinities of metal and impurity towards oxygen, Method is known as cupellation because impure

metal is fused in small boat shaped dishes of boneash or cement called cupels. This method is useful for removal of Pb impurity from Ag and Au.

(e) Mond's process: Impure nickel is purified by this process. Ni forms Ni(CO)₄ on passing steam of CO over impure Ni at 60°-70°C which on heating in another tower at 180°C decomposes.

Impure Ni + 4CO $\xrightarrow{60^{\circ}-70^{\circ}C}$ Ni (CO)_{4(g)} $\xrightarrow{180^{\circ}C}$ Ni + 4CO_(g)

(f) Van-Arkel method: This method is used to obtain ultrapure samples of Ti, Zr, HF, Si, etc. Such metals on heating with I, gives vapours of iodides which decomposes on heating more to give ultrapure metals.

 $Ti + 2I_2 \xrightarrow{523k} TiI_{4(q)} \xrightarrow{1700k} Ti + 2I_{2(q)}$

18.6 EXTRACTION OF IRON

Both iron and tin are extracted by the carbon reduction method.



18.6.1 Extraction of Iron

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 in blown in through water-jacketed pipes called tuyers fixed in the lower part of the furnace. There is a temperature gradient as we move from the bottom (temperature about 2000 K) to the top (temperature around 500 K) of the blast furnace. The blast furnace may be broadly divided into three main parts as described hereunder.



(i) **Zone of fusion:** The lower portion where coke burns and produces CO_2 and a lot of heat is known as zone of fusion.

 $C + O_2 \rightarrow CO_2$ $\Delta H = -406 \text{ kJ/mol}$

Here, the temperature is about 1775 K. A little above this, where temperature is about 1475 K–1575 K, iron is obtained in molten form.

(ii) **Zone of heat absorption:** in the middle portion (temperature 1075K–275 K), CO₂ rising up is reduced to CO with the absorption of heat: $CO_2 + C \rightarrow 2CO \quad \Delta H = 163 \text{ kJ/mol.}$ In this portion, limestone coming from above is decomposed and the resultant lime (CaO), which acts as a flux, combines with silica (present as impurity, i.e., gangue) to form calcium silicate (fusible slag).

 $Ca CO_3 \rightarrow CaO + CO_2 CaO + SiO_2 \rightarrow Ca SiO_3$ (slag).

(iii) **Zone of reduction:** This is the upper portion (675 K–975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up the furnace: Fe₂O₃ + 3CO \rightarrow 2 Fe + 3 CO₂.

The reduction is believed to takes place in stages: $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$. $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$ Fe $O + CO \rightarrow Fe + CO_2$ 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. Waste gases escaping at the top consists of about 30 per cent CO, 10 per cent CO₂ and the rest nitrogen. Iron obtained from the blast furnace is known as pig iron.

18.6.2 Types of Iron

Following are the commercial varieties of iron depending on the percentage of carbon content.

- (i) Cast iron: It is the most impure form of iron containing the highest percentage of carbon (2.5 to 5 per cent) and about 2 per cent of other impurities like Si, P, Mn and S. Cast iron is of two types as listed hereunder.
 - 1. White cast iron: Carbon is present in the form of cementite, Fe₃C.
 - 2. Grey cast iron: Carbon is present in the form of graphite.

Properties of cast iron:

- (a) Due to the presence of impurities, cast iron melts at 1250°C, whereas pure iron melts at 1530°C.
- (b) The molten cast iron expands on solidification and thus produces good castings.
- (c) It does not rust easily. It is neither tempered nor magnetized easily.
- (d) It is hard and brittle due to high carbon content and cannot be welded.
- (e) Due to very little ductility, it is not suitable for forging.
- (f) It is used for casting, railing, hot water pipe, electric poles, etc. where strain is minimum.
- (ii) **Wrought iron:** It is the purest form of iron containing the lowest percentage of carbon from 0.1 to 0.25 per cent and 0.3 per cent as other impurities. It is manufactured from cast iron by puddling process in a special type of reverberatory furnace, the hearth of which is lined with hematite (Fe₂O₃).

(iii) Properties of wrought iron:

- 1. Wrought iron is extremely tough, highly malleable and ductile and has high magnetic permeability.
- 2. It softens at about 1000°C and then it can be forged and welded.
- 3. Due to the presence of very small percentage of slag, it has fibrous structure and thus can withstand high stresses.
- 4. Wrought iron is resistant towards rusting and corrosion.
- (iv) Uses of wrought iron: Wrought iron is used
 - 1. In the manufacture of articles capable to hold sudden stress, e.g., chains, nails, hooks, bolts, etc.
 - 2. In the manufacture of electromagnet and agricultural implements.
 - 3. In making wires and bars.

18.6.3 Steel

The most important commercial variety of iron having percentage of carbon in midway between that of cost iron and wrought iron, i.e., 0.25 to 2 per cent. The properties of steel depend upon its carbon contents, since with the increase in carbon content, the hardness of steel increases while its ductility decreases. The presence of Si gives steel a fibrous structure. Presence of Mn produces elasticity and increases tensile strength. Cr imparts resistance to chemical action.

1. Alloy steel: Steel mixed with small amounts of nickel, cobalt, chromium, tungsten, molybdenum, manganese, etc., acquires special properties. Such products are called special steels or alloy steels. Some important alloy steels are given in the table hereunder.

S. No.	Name of Alloy Steel	Metal Added	Properties	Uses
1.	Invar	36 per cent Ni	Coefficient of expansion is very small	Measuring tapes and pendulums
2.	Chrome vanadium steel	1 per cent Cr, 0.15 per cent V	High tensile strength	Springs, shafts, axles, etc.
3.	Manganese steel	12–15 per cent Mn	Hard and tough	Rock crushing machinery safes, helmets, etc.
4.	Stainless steel	11.5 per cent Cr, 2 per cent Ni	Resists corrosion	Common articles
5.	Tungsten steel	14–20 per cent W, 3–8 per cent Cr	Very hard	High speed tools

18.7 MANUFACTURE OF STEEL

Manufacture of steel is made by either of the following methods.

(a) The Bessemer process: The process is carried out in Bessemer converter made up of steel plates lined with silica bricks (if impurities in cast iron are of basic nature, i.e., MnO) or lined with CaO or MgO (if impurities in cast iron are of acidic nature, i.e., P₄O₁₀ or SO₂ or SiO₂). The molten cast iron is introduced in the converter and a blast of hot air is blown through it from the bottom, keeping the mouth of the converter vertically upwards. Impurities of MnO or P or S present in cast iron are first oxidized and then combine to form slag.

 $\begin{array}{ll} \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 & 2\text{Mn} + \text{O}_2 \rightarrow 2\text{MnO} & \text{MnO} + \text{SiO}_2 \rightarrow \text{MnSiO}_3 \\ 4\text{P} + 5\text{O}_2 \rightarrow \text{P}_2\text{O}_{10} & \text{P}_4\text{O}_{10} + 6\text{CaO} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 \text{ (Thomas slag)} \end{array}$

Finally carbon is oxidized to carbon monoxide which burns with blue flame at the mouth of the converter. Some iron is also oxidized which converts the carbon into carbon monoxide.

 $4 \text{ Fe} + 3 \text{ O}_2 \rightarrow 2 \text{ Fe}_2 \text{ O}_3$ $\text{Fe}_2 \text{ O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$ When whole of the carbon is oxidised (i.e., the blue flame suddenly dies out), the air supply is stopped for a while and the requisite amount of spiegeleisen (an alloy of Fe, Mn and C) is added. The blast is continued just for a moment to ensure complete mixing. Mn and C serve as deoxidizer and reduce FeO (if any) and the rest amount of Mn and C is mixed with molten steel to give manganese steel. Mn makes steel harder and increases its tensile strength.

(b) Open Hearth process or Siemens-Martin process :

This is the modern process and the furnace used consists of an open hearth lined with silica or calcined dolomite (CaO·MgO) depending upon the nature of impurities present in pig or cast iron. Silica lining is used if the impurities are of manganese, silicon, etc. and calcined dolomite lining is used if phosphorus is present in appreciable amount.

The charge consisting of pig or cast, iron scrap, iron ore (hematite) and lime heated on the hearth of the furnace at about 1500°C by producer gas. The following reactions occur.

Acidic process: $3Si + 2 Fe_2O_3 \rightarrow 4Fe + 3SiO_2$; $3Mn + Fe_2O_3 \rightarrow 2Fe + 3 MnO$; $MnO + SiO_2 \rightarrow MnSiO_3$ (slag)

Basic process: $12P + 10 \text{ Fe}_2O_3 \rightarrow 3P_4O_{10} + 20\text{Fe}; 6\text{CaO} + P_4O_{10} \rightarrow 2\text{Ca}_3(\text{PO}_4), \text{ (slag)}$

Finally C and S are oxidized forming volatile gases: CaO + SiO₂ \rightarrow CaSiO₃ (slag) 2Fe₂O₃ + 3S \rightarrow 3SO₂ + 4Fe; Fe₂O₃ + 3C \rightarrow 3CO + 2Fe

Samples of steel drawn from time to time and tested for carbon content, finally spiegeleisen (an alloy of iron, manganese and carbon) is added to the molten mass to obtain desired steel. The process takes about 8 to 10 hours for completion, i.e., longer time than Bessemer process (20–30 minutes) but it has the following advantages over the Bessemer's process.

- (i) The temperature can be controlled as the heating is done externally.
- (ii) The composition and quality can be well controlled as it is a slow process.
- (iii) In this process, scrap iron is reused.
- (iv) The loss of iron in this process is only 4 per cent while the loss is about 15 per cent in Bessemer's process.
- (v) This yields better quality of steel.
- (c) **Duplex process:** This is actually a combination of acid Bessemer process and open hearth process. Si, Mn, S and C (partially) are oxidized and removed as slag or volatile oxides.

18.8 HEAT TREATMENT OF STEEL

- (a) **Annealing:** It is a process of heating steel to bright redness and then cooling it very slowly to make the steel soft and ductile.
- (b) **Quenching:** It is a process of heating steel to bright redness and then cooling it suddenly by plunging in water or oil to have extremely hard and brittle steel. It has very low elasticity.
- (c) Tempering: It is a process of heating the quenched steel to a temperature much below redness and then cooling it slowly. Such a steel is neither hard nor so brittle. During the process of tempering, a thin film of the oxide is formed on the surface of steel. The colour of the oxide film depends on the temperature at which the quenched steel is heated.

Temperature range (°C)	Colour of the oxide film
200°–230 °C	Yellow
225°–270 °C	Brown
300 °C	Blue

18.9 EXTRACTION OF TIN

Metallic tin is extracted from tin stone or cassiterite (SnO_2) which contains about 10 per cent of the metal as SnO₂. The rest being siliceous matter and tungstates of Fe, Cu and As.

After crushing, the ore is concentrated by washing in a current of water (gravity process to remove lighter gangue particles) and by magnetic separator to remove tungstates of Fe and Mn.

Finally, the ore is smelted in a reverberatory furnace or in a blast furnace at 1475–1575 K. The ore is mixed with one-fifth of its mass of powdered anthracite (coal) and little of lime or fluorspar which is used as flux. Tin oxide is reduced to tin.

 $SnO_2 + 2 C \rightarrow Sn + 2CO$

18.9.1 Refining of Tin

(i) **Liquation or sweating:** When the block of impure tin is heated on the sloping hearth of reverberatory furnace, tin along with Pb and Bi (all having much lower melting points than other metals) run off leaving a dross of an alloy of Mn, Fe, Cu, W and As.

(ii) Poling: The sweated tin is stirred with logs of green wood where impurities get oxidized and scum formed is skimmed off, from where 99 per cent pure tin is obtained. Scum and dross are repurified. Slag contains 10–25 per cent Sn as SnSiO₃ because of amphoteric nature of tin. This is recovered by smelting with carbon and CaO flux at a much higher temperature.

 $SnSiO_3 + CaO + C \rightarrow Sn + CaSiO_3 + CO$

(iii)	Electrolytic refining:	
	Cathode:	Pure tin
	Anode:	Impure tin
	Electrolyte:	$SnSO_{4(aq)}$ with sulphuric acid and hydro fluorosilicic acid.

18.10 EXTRACTION OF COPPER

Both Cu and lead may be extracted by self-reduction method. Cu is mainly extracted from copper pyrites.

After the concentration of its ore by froth floatation process, the ore is roasted by current of air to remove arsenic, Sb and much of sulphur. The ore is then mixed with a little of coke and sand and smelted in a water jacketed blast furnace. The minor reactions that occurred during roasting continue here too. Ferrous oxide combines with sand to form a 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 Cu.



Pure copper at cathode (99.9 per cent pure)

Molten mass collected from the bottom of furnace contain large cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte. 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 and this causes removal of sulphur and arsenic oxides and ferrous oxide as slag. At the same time, Cu_2S is oxidised mostly into Cu_2O and partly into CuO and $CuSO_4$. All of these react with Cu_2S giving Cu. Finally, copper may be refined electrolytically, using an electrolyte (copper sulphate).

At anode \rightarrow Impure Cu

At Cathode \rightarrow Pure Cu

18.11 EXTRACTION OF LEAD

Pb is mainly extracted from galena. After the concentration of the ore by the froth floatation process, the ore is roasted in a reverberatory furnace.

Flow sheet for the extraction of lead



Hot conc. H_2SO_4 dissolves lead with evolution of SO_2 but the reaction becomes lower due to formation of insoluble PbSO₄.

The obtained lead contains impurities such as Cu, Ag, Bi, Sb and Sn. Ag is removed by **Parke's process**, where molten Zn is added to molten impure lead. The former is immiscible with the later. Ag is more soluble in molten Zn than in molten lead. Zn–Ag alloy solidifies earlier than molten lead and thus can be separated. After this, crude lead is refined electrolytically.

Electrolyte \rightarrow Lead silica fluoride (PbSiF₆) and hydro fluoro silicic acid (H₂SiF₆) with a little gelatin

At anode \rightarrow Crude lead At cathode \rightarrow Pure lead

18.12 EXTRACTION OF MAGNESIUM

It is commonly obtained by the electrolysis of fused magnesium chloride containing a little (25 per cent) NaCl and NaF at 700°C in an air-tight from 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 in the atmosphere of a cool gas so as to prevent the attack of atmospheric oxygen and nitrogen on Mg. Molten Mg, being lighter than the electrolyte, floats over the fused electrolyte and is withdrawn.

In **Dow's process**, Mg is recovered from sea water as magnesium chloride which is then electrolyzed using a cell as described hereunder:

(i) DOW's sea-water process: Sea water contains about 0.13 per cent Mg²⁺ ions and the extraction of Mg depends on the fact that Mg(OH)₂ is very much less soluble than Ca(OH)₂ [slaked lime]. Ca(OH)₂ is added to sea water and calcium ions dissolve and Mg(OH)₂ is precipitated. This is filtered off, treated with HCl to produce MgCl, and electrolyzed.

(ii) DOW's natural brine process:

 $\underset{(Dolomite)}{MgCO_{3}} \underbrace{ \overset{\Delta}{\longrightarrow} MgO \cdot CaO}_{(Calcine \ dolomite)} \xrightarrow{Dil. HCl} MgCl_{2(aq)} + CaCl_{2(aq)} \xrightarrow{CO_{2}} CaCO_{3}$

(iii) Electrolysis: Anhydrous carnallite (KCl·MgCl₂·6H₂O) may also be employed as the starting material of MgCl₂. The cathode may be a layer of molten lead on the floor of the cell and anode may be the graphite rod which are suspended above the molten lead. Mg liberated at the cathode dissolves in the molten lead. The alloy of Pb-Mg is subjected to electrolysis to obtain pure Mg.

Electrolyte used \rightarrow Fused carnallite

Anode \rightarrow Pb–Mg alloy

Cathode \rightarrow Steel rods

18.13 EXTRACTION OF ALUMINIUM

Al is isolated from the electrolysis of bauxite $(Al_2O_3 \cdot 2H_2O)$. Since it is difficult to purify Al, bauxite ore is purified either by Baeyer's process or Hall's process or Serpeck's process. Depending upon the impurity present in the ore, if the bauxite contains iron oxide as the impurity one can use Baeyer's or Hall's process as described hereunder:



Electrolytic reduction of Al₂O₃: After obtaining pure Al₂O₃, it is dissolved in fused cryolite (Na₃AlF₆) with a little fluorspar (CaF₂) and is electrolyzed in an iron tank lined with blocks of carbon which serve as the cathode. The anode consist of a number of graphite rods suspended vertically inside the tank. Aluminium gets settled at the bottom of the tank and can be removed.

18.14 EXTRACTION OF SILVER AND GOLD

Silver and gold are extracted by the cyanide process (MacArthur forest process).

18.14.1 Mac Arthur Forest Process

After the preliminary crushing and concentration by froth floatation process the ore (crushed auriferous rocks in the case of gold) is leached with dilute (0.4 - 7 per cent) solution of NaCN (made alkaline by adding lime and kept agitated by a current of air). Ag (or Au) pass into the solution as argento-cyanide (or aurocyanide).

Air is blown into remove Na_2S as $Na_2S_2O_3$ and Na_2SO_4 causes the above reaction to proceed to completion. The solution obtained is filtered and treated with scrap iron or zinc where Ag (or Au) gets precipitated. The obtained Ag is purified electrolytically (electrolyte is silver nitrate solution containing 1 per cent HNO₃.

At anode: Impure Ag At cathode: Pure Ag



Flow sheet for the extraction of silver

Methods of extraction of metals: A brief review

Electrode process	Standard Electrode Potential/V	Main Occurrence	Main Method of Extraction	Equation for Extraction
Na, Na+	-2.7	Rock salt NaCl, Chile saltpeter, NaNO ₃	Electrolysis of fused NaCl with CaCl ₂ added	Ţ
Mg, Mg ²⁺	-2.37	Carnallite, KCl . MgCl ₂ . 6H ₂ O, Magnesite, MgCO ₃	Electrolysis of fused MgCl ₂ with KCl added	Most of these involve electrolytic reduction $M^{n+} + ne^- \rightarrow M$
Al, Al ³⁺	-1.66	Bauxite, Al ₂ O ₃ ,2H ₂ O Silicate rocks	Electrolysis of Al_2O_3 in molten Na_3AlF_6	\downarrow
Mn, Mn ²⁺	-1.18	Pyrolusite MnO_2 Hausmannite Mn_3O_4	Reduction of oxide with Al or C	$3Mn_{3}O_{4} + 8Al \rightarrow$ $9Mn + 4Al_{2}O_{3}$
Zn, Zn ²⁺	-0.76	Zinc blende ZnS, Calamine ZnCO ₃	Reduction of ZnO with C or electrolysis of $ZnSO_4$	$ZnO + C \rightarrow Zn + CO$
Fe, Fe ²⁺	-0.44	Magnetite, $Fe_{3}O_{4}$, Haematite, $Fe_{2}O_{3}$	Reduction of oxide with CO	$Fe_{2}O_{3} + 3CO \rightarrow 2Fe + 3CO_{2}$
Sn, Sn ²⁺	-0.14	Cassiterte, SnO ₂	Reduction of SnO ₃ with C	$SnO_2 + 2C \rightarrow Sn + 2CO$
Cu, Cu ²⁺	-0.13	Galena PbS, C	Reduction of PbO with C	$PbO + C \rightarrow Pb + CO$

Continued

Electrode process	Standard Electrode Potential/V	Main Occurrence	Main Method of Extraction	Equation for Extraction
Cu, Cu ²⁺	+0.34	Copperpyrite, CuFeS ₂ Cuprite, Cu ₂ O	Partial oxidation of sulphide ore	$\begin{array}{l} 2\mathrm{Cu}_{2}\mathrm{O}+\mathrm{Cu}_{2}\mathrm{S}\rightarrow\\ 6\mathrm{Cu}+\mathrm{So}_{2}\end{array}$
Ag, Ag ²⁺	+0.80	Argentite, Ag ₂ S, occurs as metal	Special method involving use of sodium cyanide	$\begin{array}{l} Ag_2S + 4NaCN \rightarrow \\ 2NAaAg(CN)_2 + \\ Na_2S \\ 2NaAg(CN)_2 \\ + Zn \rightarrow 2Ag + \\ Na_2Zn(CN)_4 \end{array}$
Hg, Hg ²⁺	+0.85	Cinnabar, HgS	Directional reduction of HgS by heat alone	$HgS + O_2 \rightarrow Hg + So_2$
Au, Au ³⁺	+1.50	Occurs as metal	Special methods involving use of sodium cyanide	Similar to that for silver $2NaAu(CN)_2$ $+ Zn \rightarrow 2Au +$ $Na_2Zn(CN)_4$

Metals found in traces in living organisms				
From Living Organisms	Metals Obtained	From Living Organisms	Metals Obtained	
(i) Haemoglobin	Iron	(v) Eyes of cats and cows	Zn	
(ii) Blood	Sodium	(vi) Prawns	Cr	
(iii) Chlorophyll	Magnesium	(vii) Bones	Ca	
(iv) Chloroplast	Mn, Fe and Cu	(viii) Cucumbers	Vanadium	