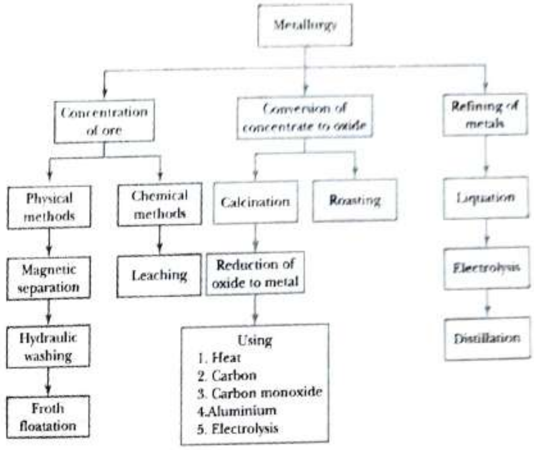
6

Metallurgy



Metallurgical processes.

Contents

Metallurgy is the subject which deals with the science and technology applied for the extraction of metals economically on a large scale from their respective ores. Another aspect of metallurgy deals with making of alloys which are metallic solutions composed of two or more elements.

To begin with we must understand the difference between a mineral and an ore.

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

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

Hence *all ores are minerals but all minerals are not ores*. For example, FeS_2 (iron pyrite) is abundantly available in the Earth's crust but cannot be used as ore of iron. The chemical reactions involved in conversion of iron pyrite to iron are:

$$2FeS_2 + \frac{11}{2}O_2 \rightarrow Fe_2O_3 + 4SO_2$$

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

The removal of S from FeS_2 to obtain iron involves high cost of production and presence of high percentage of sulphur in iron makes it brittle and thus of no use.

The impurities present in the ore are known as *gangue*. For example, silica (SiO_2) is a common impurity present in most of the ores.

6.1 | TYPES OF ORES

The different types of ores are depicted in Figure 6.1.

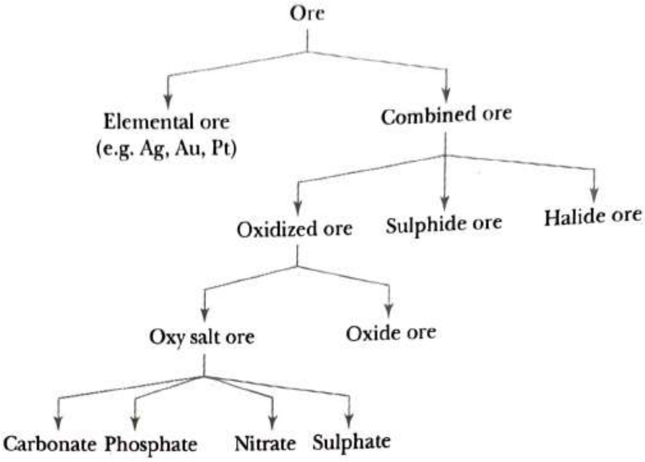


Figure 6.1 Different types of ores.

Some important ores of different types and their formulas are listed as follows.

1. **Oxide ores**

ZnO	Zincite
Fe_2O_3	Haematite
Fe_3O_4	Magnetite
$Al_2O_3 \cdot 2H_2O$	Bauxite
$Fe_2O_3 \cdot 3H_2O$	Limonite
Cu_2O	Cuprite or Ruby copper
MnO_2	Pyrolusite
SnO_2	Tinstone or Casseterite
TiO_2	Rutile
$FeCr_2O_4 (FeO + Cr_2O_3)$	Chromite ore
$Na_2B_4O_7 \cdot 10H_2O$	Borax or Tincal
$Ca_2B_6O_{11} \cdot 5H_2O$	Colemanite
U_3O_8	Pitch blende
$FeO \cdot TiO_2$	Ilmenite

2. **Sulphide ores**

PbS	Galena
HgS	Cinnabar
ZnS	Zinc blende or Sphalerite
Cu_2S	Copper glance or Chalcocite
$CuFeS_2$	Copper pyrite or Chalcopyrite
FeS_2	Iron pyrite or Fool's gold
Ag_2S	Silver glance or Argentite

3. **Halide ores**

$NaCl$	Rock Salt
KCl	Sylvine
CaF_2	Fluorspar

Na_3AlF_6	Cryolite
$AgCl$	Horn silver
$KCl \cdot MgCl_2 \cdot 6H_2O$	Carnalite
$Cu_2Cl(OH)_3$	Atacamite

4. **Oxy salt ores**
   a. Carbonate ores

$CaCO_3$	Limestone
$MgCO_3$	Magnesite
$CaCO_3 \cdot MgCO_3$	Dolomite
$FeCO_3$	Siderite
$ZnCO_3$	Calamine
$Cu(OH)_2 \cdot CuCO_3/Cu_2(OH)_2CO_3$	Malachite or Basic copper carbonate
$Cu(OH)_2 \cdot 2CuCO_3$	Azurite
$PbCO_3$	Cerrusite

   b. Sulphate ores

$CaSO_4 \cdot 2H_2O$	Gypsum
$MgSO_4 \cdot 7H_2O$	Epsom salt
$PbSO_4$	Anglesite
$BaSO_4$	Baryte
$Na_2SO_4 \cdot 10H_2O$	Glauber Salt
$CuSO_4 \cdot 5H_2O$	Chalcanthite

   c. Nitrate ores

KNO_3	Indian saltpeter
$NaNO_3$	Chile saltpeter

6.2 | PRINCIPAL STEPS IN THE RECOVERY OF A METAL FROM ITS ORE

The various steps involved in the recovery of a metal from its ore are listed as follows:

1. Concentration of ore or dressing of ore.
2. Conversion of concentrated ore into a suitable form for reduction, mostly into an oxide depending on the nature and chemical characteristics of ore, i.e. *calcination* and *roasting*.
3. Production of metal by reduction.
4. Purification and refining of metal.
5. Process of pollution control for treating waste gases/materials.

These steps are discussed in detail in the following sections.

6.3 | CONCENTRATION OR DRESSING OF ORE

This process can be carried out by two methods of separation – physical and chemical.

1. Physical methods of separation:
   a. Gravity separation or levigation.
   b. Magnetic separation.
   c. Froth floatation.
2. Chemical methods of separation, i.e. leaching.

Gravity separation or levigation

This technique utilizes the density difference between the ore and impurity to concentrate the ore. It is mainly applicable to oxide ores. For example, SnO_2, Fe_2O_3 and $FeCr_2O_4$ are concentrated by this method from siliceous impurities.

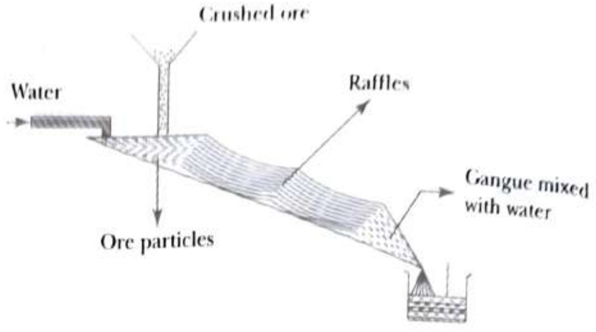


Figure 6.2 Representation of gravity separation using Wilfley table.

In gravity separation the crushed ore is washed by a current of water on a sloping table fitted with a series of corrugated boards known as Wilfley table (Figure 6.2). The table is continuously vibrating as a result of which the lighter particles move downwards and the heavier particles are left behind the corrugations (as barriers).

A suitable arrangement is made to remove the heavier particles continuously, otherwise the separation process will become ineffective after some time as heavier and lighter particles will start passing the barrier together.

Magnetic separation

Generally this method is used to separate the magnetic impurities from the non-magnetic ore. For example, tin stone (SnO_2) is separated from magnetic impurity wolframite ($FeWO_4$ + $MnWO_4$ (minor)) by this method. In magnetic separation powdered ore is allowed to move towards magnetic roller and fall downwards. The magnetic material makes a new heap because it is held to the roller for a longer time (Figure 6.3).

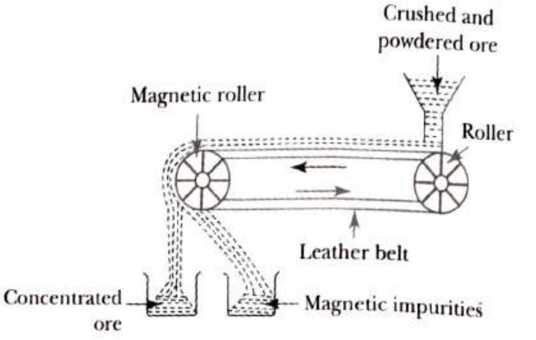


Figure 6.3 Representation of magnetic separator.

Froth floatation or oil floatation

This process is used to separate the hydrophobic mineral from the hydrophilic impurity in the ore. It is based upon the differential wetting of the ore by oil and the impurity by water.

In this process, the ore is ground to fine powder and mixed with water to form a slurry. The slurry is made hydrophobic by addition of oily components such as pine oil, eucalyptus oil, crude coal tar, cresols, etc. Air is bubbled through the mixture of hydrophobic mineral and hydrophilic gangue parts of the ore. The gangue acts as an agitator and creates bubbles. The hydrophobic part rises with the froth by attaching to the air bubbles. It is removed from the surface and the mineral is purified further.

The oil added acts as frothing agent. It reduces the surface tension of water and helps to produce a stable froth. Reagents such as aniline or cresol are used to stabilize the froth. The formation of bubble involves an increase in air–water surface that means doing work against surface tension. The energy

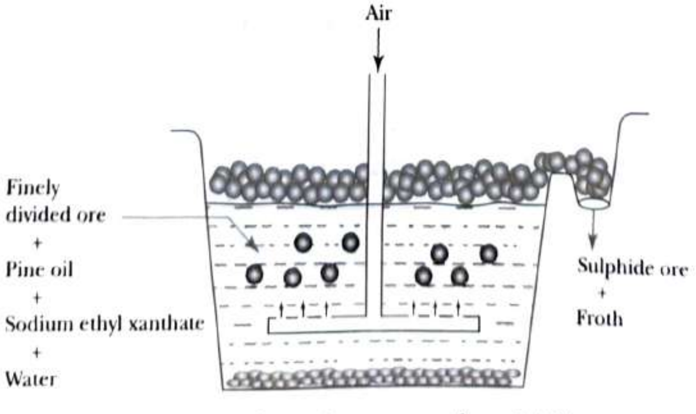
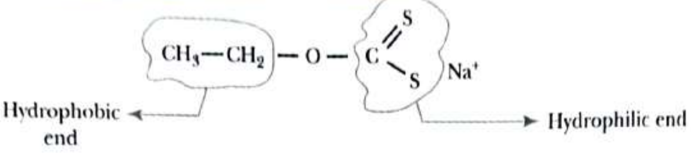


Figure 6.4 Froth floatation process for sulphide ore.

required to create a bubble of radius r is $2 \times 4\pi r^2 \times E$, where E is the energy required to create unit surface area and, is directly proportional to surface tension.

The froth floatation process is usually applied for sulphide ores and the schematic representation is shown in Figure 6.4. Sodium ethyl xanthate acts as a collector of sulphide ore.



The hydrophobic end prefers to stay in air and hydrophilic end prefers to stay in water. Since the molecule has both hydrophobic and hydrophilic part, the best place for it to stay is the air–water interface and hence it shows floating characteristics. The hydrophilic end attracts the sulphide particles and forms surface coated particles as shown Figure 6.5.

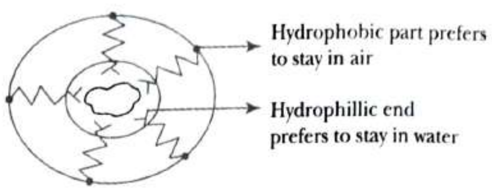
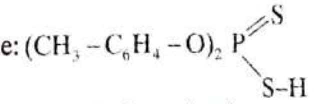
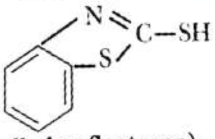


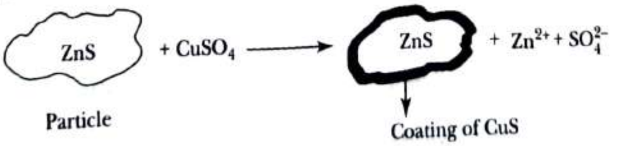
Figure 6.5 Sodium ethyl xanthate at the air-water interface.

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

1. The other alkyl groups in xanthate may be amyl ($C_5H_{11}-$), octyl ($C_8H_{17}-$), etc. instead of the ethyl group.
2. The other collectors that may be used are
   - a. Sodium lauryl sulphate: $C_{12}H_{25}-O-SO_3^- Na^+$
   - b. Trimethyl cetyl ammonium bromide: $C_{16}H_{33}N^+(Me)_3\}Br^-$
   - c. Dicresyl dithiophosphate: 
     $(CH_3-C_6H_4-O)_2P(=S)-S-H$
     (also called aerofloat)
   - d. Mercaptobenzthiazole: 
     (also called as floatogen)

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

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



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

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

$$PbS(s) + NaCN/KCN \rightarrow \text{No reaction}$$

$$ZnS(s) + 4[NaCN/KCN] \rightarrow [Zn(CN)_4]^{2-} + 4[Na^+/K^+] + S^{2-}$$

Chemical method of separation: Leaching

It is the process by which the required substance (may be the metal component of impurities) is dissolved out from the ore by using a suitable reagent. For example,

1. Al_2O_3 is dissolved from red bauxite by using 40% NaOH.

$$Al_2O_3 + \underbrace{Fe_2O_3 + SiO_2 + TiO_2}_{\text{impurity}} + NaOH + H_2O \rightarrow \text{impurity} + \underset{\text{soluble complex}}{Na^+[Al(OH)_4]^-}$$

2. Ag_2S is dissolved out from silver glance (Ag_2S + impurity) by using NaCN solution in the presence of air.

$$Ag_2S + 4NaCN \rightarrow 2[Ag(CN)_2]^- + 4Na^+ + S^{2-}$$

3. In Sn extraction, the removal of impurities like FeS_2 and Cu_2S also involves application of the leaching process. These two sulphides are roasted carefully to produce soluble sulphates that are washed out with hot water.

6.4 | CONVERSION OF CONCENTRATED ORE INTO ITS OXIDE

This is generally carried out by two methods—calcination and roasting.

Calcination

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in the absence of air (or limited supply of air).

1. This process is mainly used for a carbonate ore to get its oxide

$$\text{Metal carbonate} \xrightarrow{\Delta} \text{Metal oxide} + CO_2 \uparrow$$

2. Hydrated ores or hydroxides become anhydrous by calcination. For example,

$$\underset{\text{Limonite}}{Fe_2O_3 \cdot 3H_2O} \xrightarrow{\Delta} Fe_2O_3 + 3H_2O \uparrow$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O \uparrow$$

3. Impurities like S, As and Sb are removed in the form of their elemental vapours by calcination.
4. The products formed by calcination are always porous.

Roasting

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in presence of excess of air.

1. This process is mainly applicable for sulphide ores to get the corresponding metal oxides.

$$\text{Metal sulphide} + O_2 \rightarrow \text{Metal oxide} + SO_2 \uparrow$$

2. Sometimes the lower oxidation state oxide gets converted into higher oxidation state oxide. For example,

$$2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3$$

3. Hydrated ores become anhydrous through roasting.
4. The impurities like organic matter, S and As are removed by roasting in the form of their volatile oxides, i.e. ($CO_2 + H_2O$), SO_2 and As_2O_3 respectively.
5. The products formed by roasting are always porous.

6.5 | DIFFERENT REDUCTION PROCESSES

Carbon reduction

This process is used for commercial extraction of Fe, Sn, Zn, Pb.

$$\text{Roasted or Calcined ore} + \underset{\text{(as reducing agent)}}{\text{Coke powder}} + \text{Flux} \longrightarrow \text{Molten metal} + \text{Slag}$$

This process is also known as smelting, but smelting does not always require that the reduction has to take place in that step. For example, in extraction of Cu, smelting is done without any reduction of ore. The roasted or calcined ore must be porous because the porous mass makes larger surface area available for reduction and improves the rate of reduction.

Flux is an impurity added externally to remove the impurity already present within the ore.

$$\text{Gangue} + \text{Flux} \rightarrow \text{Slag}$$

The choice of flux depends upon the nature of impurity/gangue present within the ore.

1. If the impurity is acidic (such as SiO_2), flux must be basic, e.g. CaO, MnO, etc.
2. If the impurity is basic (such as MnO, FeO), flux must be acidic, e.g. SiO_2 or P_2O_5.

The slag formation in carbon reduction is a kind of acid–base reaction according to the Lux–Flood acid–base concept which defines acids and bases as oxide/anion acceptors and oxide/anion donors respectively. For example,

1. $\underset{\substack{\text{oxide donor}\\\text{(base)}}}{CaO} + \underset{\substack{\text{oxide acceptor}\\\text{(acid)}}}{SiO_2} \rightarrow \underset{\text{slag}}{Ca^{2+}|SiO_3^{2-}}$

2. $\underset{\text{base}}{LiCl} + \underset{\text{acid}}{AlCl_3} \rightarrow Li^+[AlCl_4]^-$

The carbon reduction process is applicable for

1. Direct reduction of oxide ore. For example,
   - **a.** $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\uparrow$
     $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2\uparrow$
   - **b.** $SnO_2 + 2C \rightarrow Sn + 2CO\uparrow$
     $SnO_2 + 2CO \rightarrow Sn + 2CO_2\uparrow$
2. Indirect reduction of sulphide, carbonate and sulphate ores. For example,
   - **a.** Sulphide ores are roasted first and then reduced by coke.
     $$ZnS \xrightarrow{\text{roasting}} ZnO \xrightarrow{\text{coke}} Zn$$
   - **b.** Carbonate ores are calcined first and then reduced by coke.
     $$ZnCO_3 \xrightarrow{\text{calcined}} ZnO \xrightarrow{\text{coke}} Zn$$
   - **c.** Sulphate ores is initially reduced to sulphides, e.g.
     $$PbSO_4 + 4C \rightarrow 2PbS + 4CO\uparrow$$
     and then different possibilities are there to get molten metal.

1. $PbS + PbSO_4 \rightarrow 2Pb + 2SO_2\uparrow$
   $PbS + \frac{3}{2}O_2 \rightarrow PbO + SO_2\uparrow$
   $PbS + 2PbO \rightarrow 3Pb + SO_2\uparrow$
2. $PbO + C \rightarrow Pb + CO$
   $PbO + CO \rightarrow Pb + CO_2$

Note: The chief reducing agent for carbon reduction process is CO(g) and not C(s) because the interaction between oxide ore(s) and CO(g) is much higher as compared to that between the oxide ore and C(s).

Self reduction

This method is applicable to some of the sulphides, e.g. PbS, Cu_2S and HgS. It does not involve use of reducing agent from an external source. Here the sulphide ore is partially roasted into its oxide, which in turn reacts with unreacted sulphide to produce molten metal. For example,

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \uparrow$$

Another side reaction takes place, which is as follows

$$PbS + 2O_2 \rightarrow PbSO_4$$

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \uparrow$$

Thermite reduction (or Goldschmidt-Thermite process)

The metal oxides having very high melting points, e.g. the oxides of Cr, Mn, Ti, Mo, Fe, etc., are very difficult to reduce by carbon reduction method. These can be reduced by thermite reduction method using Al powder as reducing agent. For example,

$$3Mn_3O_4(s) + 8Al(s) \rightarrow 9Mn(l) + 4Al_2O_3(s)$$

$$3TiO_2(s) + 4Al(s) \rightarrow 3Ti(l) + 2Al_2O_3(s)$$

$$Cr_2O_3(s) + 2Al(s) \rightarrow 2Cr(l) + Al_2O_3(s)$$

$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$$

All these reactions are highly exothermic in nature. Here Al is chosen as reducing agent due to its very high oxygen affinity. Since the formation of Al_2O_3 is exothermic in nature, it helps keep the temperature very high and thus the metal produced comes out in molten state.

The reaction of Fe_2O_3 is not used for commercial production of Fe. Primarily it is used in thermite-welding for rail road joining all over the world due to flexibility of its use anywhere. In this process, magnesium ribbon/tape is ignited and it carries the fire up to the ignition mixture, which burns together to provide

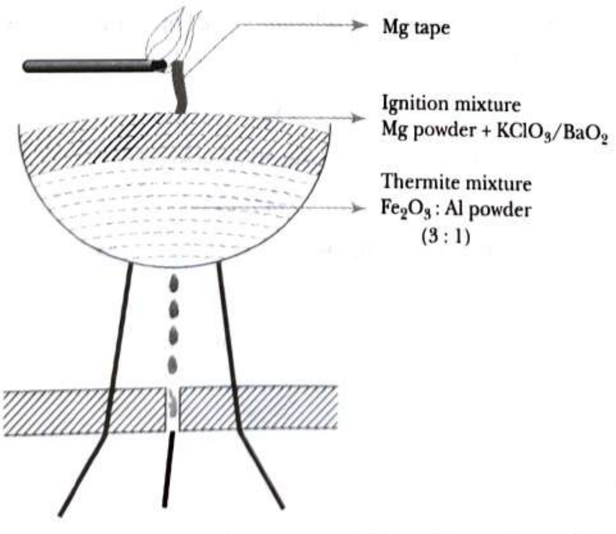


Figure 6.6 Diagrammatic representation of thermite welding.

the activation energy required for the reaction (Figure 6.6). $KClO_3$ or BaO_2 provides O_2 from each and every part of mixture and helps the ignition mixture to burn together.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
$$2BaO_2 \rightarrow 2BaO + O_2$$

Metal replacement method (Hydrometallurgy)

In this process, the desired metal is extracted from its solution by the addition of a more electropositive metal. The fuel cost is nil in this process because the reduction process takes place at room temperature or slightly higher temperature. Using this process, Ag, Au and Cu are precipitated from their respective solutions as follows:

$$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag \downarrow$$
$$2[Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Au \downarrow$$
$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu \downarrow$$

Electrolytic reduction

The oxides of strong electropositive metals such as K, Ca, Na, Al and Mg are very stable. It is difficult to reduce them into metallic state by carbon reduction process because of the following reasons.

1. The temperature requirement is very high so the fuel cost is high.
2. The collection of metals is to be done very carefully under inert environment, otherwise the metals react with air to form their respective oxides again.
3. At high temperatures, the metals being extracted may also form carbides in the presence of excess carbon taken for carbon reduction.

Such metals are extracted by passing electricity through their fused chlorides or oxides or hydroxides. For example,

1. Na is extracted from molten NaCl or molten NaOH.

$$\begin{array}{r|l} NaCl \rightarrow Na^+ + Cl^- & NaOH \rightarrow Na^+OH^+ \\ \text{At the cathode: } Na^+ + e \rightarrow Na & \text{At cathode: } Na^+ + e \rightarrow Na \\ \text{At the anode: } 2Cl^- \rightarrow Cl_2 + 2e & \text{At anode: } OH^- \rightarrow OH + e \\ & 4OH \rightarrow 2H_2O + O_2 \uparrow \end{array}$$

2. Al is extracted from molten Al_2O_3 (details will be discussed in the individual extraction).

   Note: Aqueous solution cannot be used as electrolyte here because then these electropositive metals will react again with H_2O to liberate H_2 at the cathode.

3. The metals which come below Al in the electrochemical series can be extracted by the electrolysis of the aqueous solutions of their salts. This process is applicable for Cu, Zn, Sn, Pb, etc. For example, $ZnSO_4$ solution can be used to get Zn

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$$

The electrode used is Zn or Al (as cathode) and the reaction at the cathode is

$$Zn^{2+} + 2e \rightarrow Zn$$

Similarly, $CuSO_4$ and $SnSO_4$ solutions are used to get Cu and Sn respectively.

Thermal decomposition method

Some of the metal oxides are thermally unstable and thermal decomposition is utilized to get metals from these oxides. For example,

$$HgO \xrightarrow{400\,^\circ C} Hg + \frac{1}{2}O_2$$

$$Ag_2O \xrightarrow{300\,^\circ C} 2Ag + \frac{1}{2}O_2$$

6.6 | PURIFICATION OR REFINING OF METAL

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

Thermal refining

Oxidation by air and poling

This process is applicable for refining of Cu and Sn. In this process, the crude metal is melted and air is blasted through the melt. After air is blown, the melt is stirred with a raw wooden pole and its unburnt condition produces sufficient amount of carbon and CO to reduce the metallic oxide formed and yield refined metal. A coke powder layer is maintained at the top of the surface to prevent reoxidation of the metal formed (Figure 6.7). A small amount of metal to be refined, however, may get oxidized in this process.

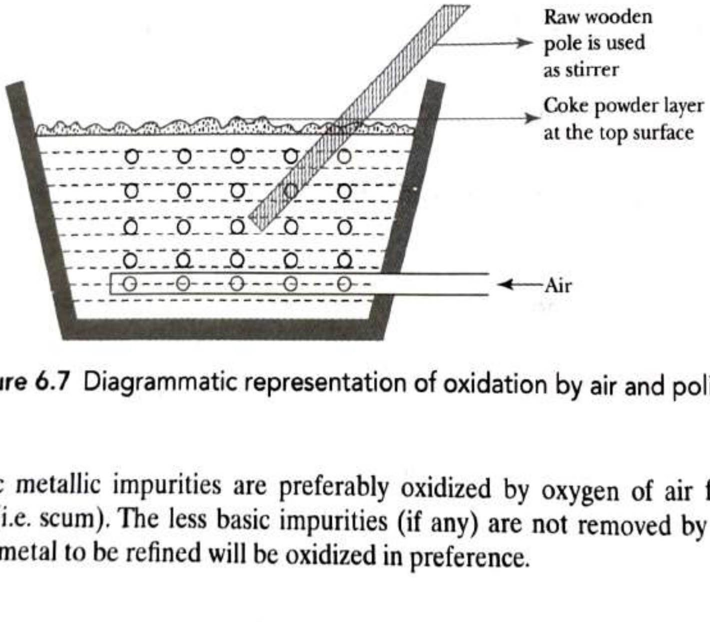
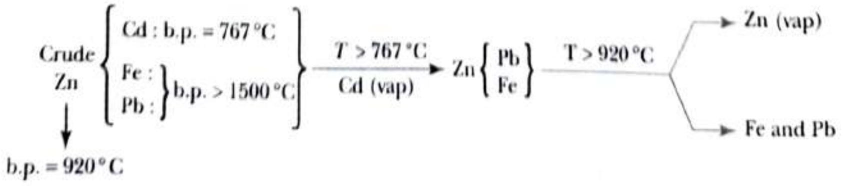


Figure 6.7 Diagrammatic representation of oxidation by air and poling.

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

Fractional distillation

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



At temperature >767 °C, Cd separates as vapours; and at temperature >920 °C, pure Zn separates as vapours leaving behind Fe and Pb impurities in the melt.

Liquation

This method is applicable for metals, such as Sn, Pb and Bi, which have low melting points as compared to their impurities. In this method, the block of crude metal is kept at the top of the sloping furnace and heated just above the melting point of the metal to be refined. The pure metal melts and flows down the sloping hearth and gets collected in a receiver at the bottom of the slope (Figure 6.8). The perforated block of impurity is thrown later.

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

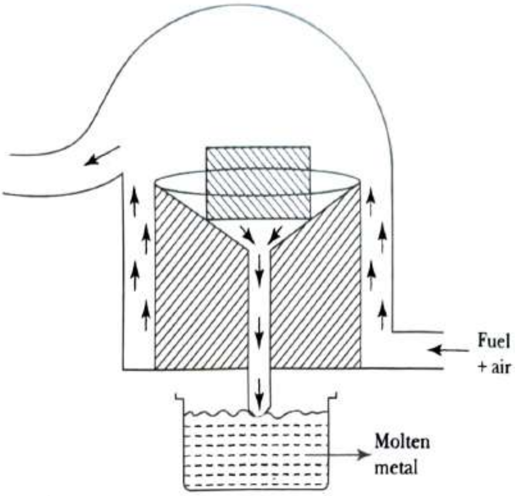


Figure 6.8 Diagrammatic representation for liquation.

Zone refining

Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultrapurification because it results in impurity level decreasing to ppm level.

Zone refining is based upon fractional crystallization as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod (Figure 6.9) and producing a thin zone throughout the cross-sectional area as shown in Figure 6.10.

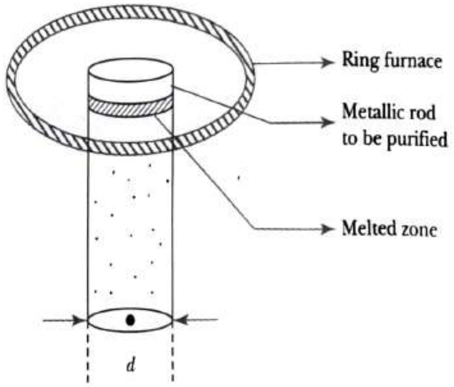


Figure 6.9 Metal rod heated by ring furnace.

It is desirable that the diameter of the rod, *d* is small enough to give a uniform melt.

When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly together with the melted zone (Figure 6.11). The furnace is then switched off, cooled down and taken to the top again for repetition of the process. Almost all impurity sweeps out to the bottom after several repetitions of the process.

Figure 6.10 Cross-sectional view of the metal rod.

Vapour phase refining

The two essential criteria for the zone refining process are listed as follows:

1. The intermediate compound formed has to be volatile.
2. The intermediate compound formed has to be relatively unstable, i.e. it should decompose on heating at practically achievable temperature.

   This refining technique is used in the following purification processes.

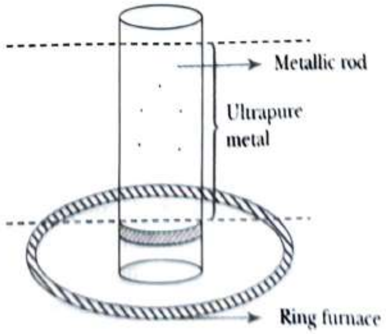


Figure 6.11 Ring furnace moving down the metal rod.

a. Mond's process for purification of nickel

$$\underset{\text{impure}}{Ni(s) + 4CO(g)} \xrightarrow{50\text{-}60^\circ C} \underset{\text{volatile}}{Ni(CO)_4(g)} \xrightarrow{150\text{-}180^\circ C} \underset{\text{pure}}{Ni(s)} + \underset{\text{recycled}}{4CO(g)}$$

If $Ni(CO)_4$ is not volatile, it cannot be separated from impurities, so its volatile nature helps to free it from impurities. Also $Ni(CO)_4$ needs to undergo thermal decomposition easily, otherwise it cannot produce pure metal.

b. Van–Arkel–de Boer process for purification of zirconium, boron and titanium

$$\underbrace{\text{Zr or Ti}}_{\text{impure}} \xrightarrow[250^\circ C]{I_2(\text{vap})} \underbrace{ZrI_4 \text{ or } TiI_4}_{\text{volatile}} \xrightarrow[\text{on tungsten filament}]{1400^\circ C} \underbrace{Zr(s) \text{ or } Ti(s)}_{\text{pure}} + \underset{\text{recycled}}{2I_2(g)}$$

Electrorefining

This method is applicable for purification of Cu, Zn, Sn, Ag, Au, Ni, Pb and Al. The cathode is made of thin strip of pure metal (same as that to be refined) and the anode is made of large slab of impure metal (to be refined). The electrolyte is the aqueous solution of suitable salt of the metal (to be refined) or the melt of oxide/salt sometimes (Figure 6.12).

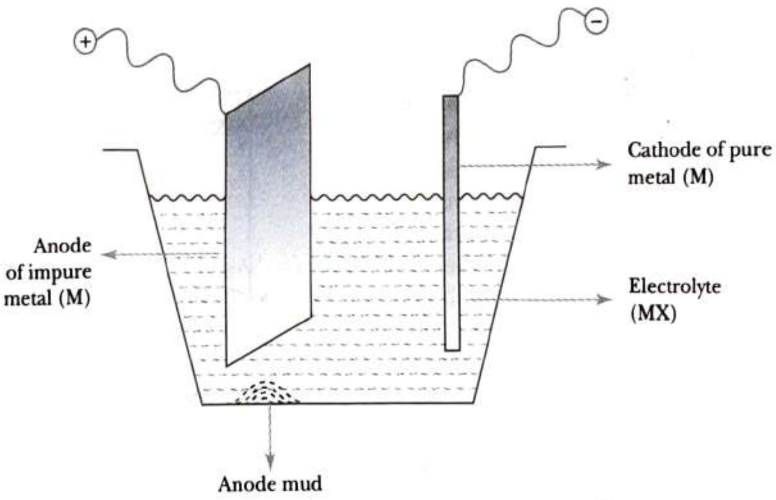


Figure 6.12 Diagrammatic representation of electrorefining.

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

Reactions at the electrodes:

At cathode : $M^{n+} + ne \rightarrow M$

At anode : (i) $M \rightarrow M^{n+} + ne$ (wanted)

(ii) $X^{n-} \rightarrow \frac{1}{2}X_2 + ne$ (unwanted)

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

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

The metallic impurities having lower oxidation potential than that of the metal to be refined are separated in the form of anode mud at the bottom.

The suitable electrolytes used in general for respective metals are:

Cu: $CuSO_4$ solution
Zn: $ZnSO_4$ solution
Sn: $SnSO_4$ solution
Ag: $AgNO_3$ solution
Au: $AuCl_3$ solution
Ni: $Ni(NO_3)_2$ solution
Pb: $PbSiF_6$ solution
Al: $(Al_2O_3 + Na_3AlF_6)$ melt + BaF_2

6.7 | THEROMODYNAMICS OF REDUCTION PROCESS

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition (Table 6.1), involves a number of points which merit detailed discussion.

Table 6.1 Reduction potentials and extraction methods

Element		$E°$ (V)	Materials	Extraction method
Lithium	$Li^+ \mid Li$	−3.05	LiCl	Electrolysis of fused salts, usually chlorides
Potassium	$K^+ \mid K$	−2.93	KCl, [KCl, $MgCl_2$, $6H_2O$]	
Calcium	$Ca^{2+} \mid Ca$	−2.84	$CaCl_2$	
Sodium	$Na^+ \mid Na$	−2.71	NaCl	
Magnesium	$Mg^{2+} \mid Mg$	−2.37	$MgCl_2$, MgO	Electrolysis of $MgCl_2$ High temperature reduction with C
Aluminium	$Al^{3+} \mid Al$	−1.66	Al_2O_3	Electrolysis of Al_2O_3 dissolved in molten $Na_3[AlF_6]$
Manganese	$Mn^{2+} \mid Mn$	−1.08	Mn_3O_4, MnO_2	Reduction with Al Thermite process
Chromium	$Cr^{3+} \mid Cr$	−0.74	$FeCr_2O_4$	
Zinc	$Zn^{2+} \mid Zn$	−0.76	ZnS	Chemical reduction of oxides by C Sulphides are converted to oxides then reduced by C, or sometimes H_2
Iron	$Fe^{2+} \mid Fe$	−0.44	Fe_2O_3, Fe_3O_4	
Cobalt	$Co^{2+} \mid Co$	−0.27	CoS	
Nickel	$Ni^{2+} \mid Ni$	−0.23	NiS, $NiAS_2$	
Tin	$Sn^{2+} \mid Sn$	−0.14	SnO_2	
Lead	$Pb^{2+} \mid Pb$	−0.13	PbS	
Copper	$Cu^{2+} \mid Cu$	+0.35	Cu(metal), CuS	Found as native metal, or compounds easily decomposed by heat (Also cyanide extraction)
Silver	$Ag^+ \mid Ag$	+0.80	Ag(metal), Ag_2S, AgCl	
Mercury	$Hg^{2+} \mid Hg$	+0.85	HgS	
Gold	$Au^{3+} \mid Au$	+1.38	Au(metal)	

For a spontaneous reaction, the free energy change ΔG must be negative.

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

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:

$$M + O_2 \rightarrow MO$$

Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently, gases have a higher entropy than liquids or solids. In this reaction S the entropy or randomness decreases, and hence ΔS is negative. Thus if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, then ΔG becomes less negative. *Thus the free energy change increases with an increase of temperature.*

The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals to their oxides. This graph is shown in Figure 6.13 and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

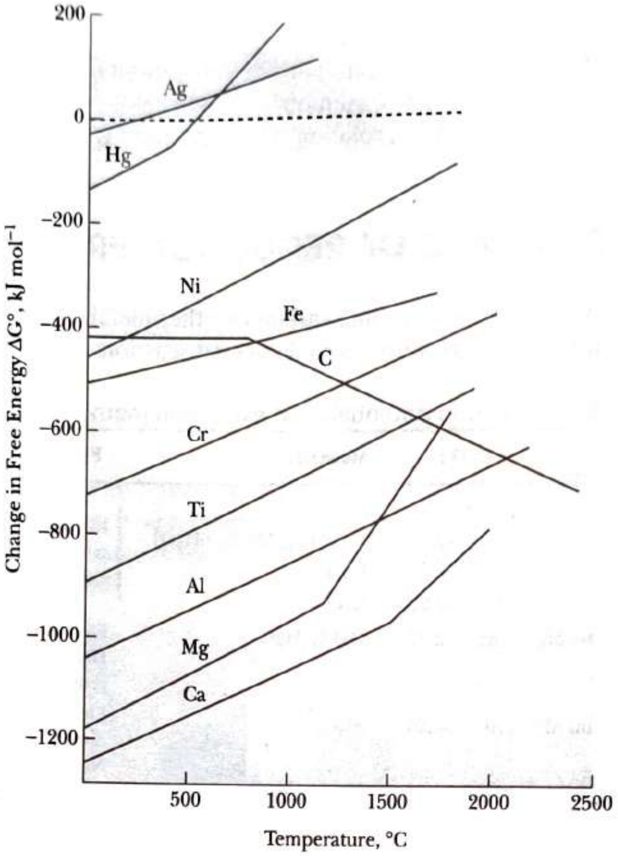


Figure 6.13 Ellingham diagram showing the change in free energy ΔG with temperature for oxides (based on 1 g mol of dioxygen in each case).

The Ellingham diagram for oxides shows several important features:

1. The graphs for metal to metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.
2. All the free energy changes follow a straight line unless the materials melt or vaporize, when there is a large change in entropy associated with the change of state, which changes the slope of the line (for example, the Hg–HgO line changes slope at 356 °C when Hg boils, and similarly Mg–MgO changes at 1120 °C).
3. When the temperature is raised, a point will be reached where the graph crosses the $\Delta G = 0$ line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, the oxide becomes unstable, and should decompose into the metal and dioxygen.

   Theoretically all oxides can be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained. In practice the oxides of Ag, Au and Hg are the only oxides which can be decomposed at temperatures which are easily attainable, and these metals can therefore be extracted by thermal decomposition of their oxides.
4. In a number of processes, one metal is used to reduce the oxide of another metal. Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the difference between the two graphs at that particular temperature. Thus Al reduces FeO, CrO and NiO in the well known thermite reaction, but Al will not reduce MgO at temperatures below 1500 °C.

In the case of carbon reacting with dioxygen, two reactions are possible:

$$C + O_2 \rightarrow CO_2$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO$$

In the first reaction, the volume of CO_2 produced is the same as the volume of O_2 used, so the change in entropy is very small, and ΔG hardly changes with temperature. Thus the graph of ΔG against T is almost horizontal.

The second reaction produces two volumes of CO for every one volume of dioxygen used. Thus ΔS is positive, and hence ΔG becomes increasingly negative as T increases. Consequently, the line on the Ellingham diagram slopes downwards (Figure 6.14). The two lines for $C \rightarrow CO_2$ and $C \rightarrow CO$ cross at about 710 °C. Below this temperature, the reaction to form CO_2 is energetically more favourable, but above 710 °C the formation of CO is preferred.

Carbon is extensively used to reduce iron oxide in the extraction of iron, but it may also be used to reduce any of the other oxides above it on the Ellingham diagram. Since the ΔG line slopes downwards it will eventually cross and lie below all the other graphs for metal/metal oxide. Thus in principle carbon could be used to reduce any metal oxide if a sufficiently high temperature were used. At one time MgO was reduced by C at 2000 °C, followed by shock (i.e. rapid) cooling, though this process is now obsolete. Similarly the reduction of very stable oxides like TiO_2, $A1_2O_3$ and MgO is theoretically possible, but is not attempted because of the high cost and practical difficulties of using extremely high temperatures. A further limitation on the use of carbon for extracting metals is that at high temperatures many metals react with carbon, forming carbides.

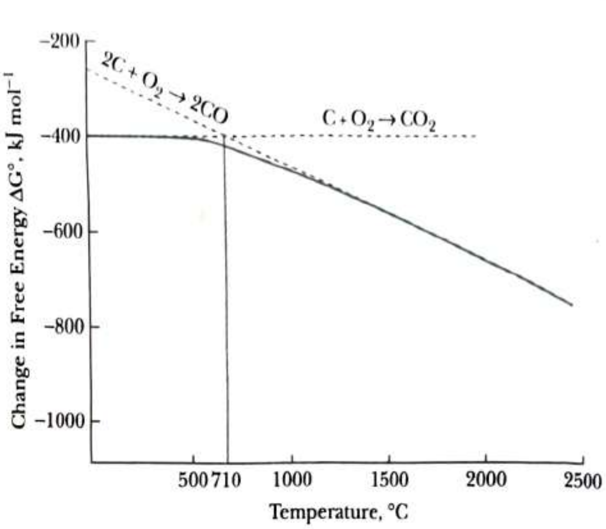


Figure 6.14 Ellingham diagram for carbon. (The composite curve is the solid line.)

Many metals occur as sulphide ores. Though carbon is a good reducing agent for oxides, it is a poor reducing agent for sulphides. The reason why carbon reduces so many oxides at elevated temperatures is that the $\Delta G°/T$ line for CO has a negative slope. There is no compound CS analogous to CO with a steep negative $\Delta G°/T$ line. Thus sulphides are normally roasted in air to form oxides before reducing with carbon.

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2$$

In a similar way hydrogen is of limited use as a reducing agent for extracting metals from their oxides since the $\Delta G°/T$ line has a positive slope, and runs parallel to many metal oxide lines.

$$2H_2 + [O_2] \rightarrow 2H_2O$$

Thus only those metals with metal → metal oxide lines above the hydrogen line will be reduced, and this does not change with temperature. A further problem with H_2 is that many metals react with hydrogen, forming hydrides, and if hydrogen remains dissolved in the metal (interstitial hydrides) it significantly affects the properties of the metal.

Thermodynamic arguments about what will reduce a given compound have two limitations. They assume that the reactants and products are in equilibrium, which is often untrue, and they indicate whether a reaction is possible but do not predict the rate of reaction, or if some alternative reaction is even more favourable.

6.8 | ALLOYS AND AMALGAMS

In general an alloy is a homogeneous metallic material which contains two or more metals as a solid solution, and if one of the constituents of the alloy is mercury, it is called amalgam.

Classification of alloys

Alloys are classified as

1. **Ferrous alloys:** If the alloy has iron as one of its constituents, it is called a ferrous alloy, e.g. stainless steel (Cr + Fe + Ni), ferrosilicon (Fe + Si), etc.
2. **Non-ferrous alloys:** The alloy which does not contain iron is called a non-ferrous alloy, e.g. brass (Cu + Zn), bell metal (Cu + Sn), solder (Sn + Pb), etc.

Characteristics of alloys

Alloys are prepared to develop some specific properties which are not found in the constituent elements. Both physical and chemical properties of an alloy differ considerably from those of its constituents. Some properties of metals that can be improved by preparing alloys are as follows:

1. **Superior casting:** Formation of alloys increases the casting property of the metal. For example, Type metal (Pb-80% + Sb-16% + Sn-4%) contains Sb which expands on solidification and consequently it takes a sharp impression of the mould. Hence it improves the casting property of lead.
2. **Hardness:** Alloys are harder than non-metals and metals from which they are made. For example, steel is harder than cast iron.
3. **Resistance to corrosion:** Alloys are more resistant towards corrosion, e.g. stainless steel is more resistant towards corrosion than iron.
4. **Melting point:** Alloys have low melting points as compared to their constituent elements.
5. **Tenacity:** The tenacity of copper is doubled on addition of 5% silicon to it.

Preparation of alloys

The methods utilized for preparation of alloys are described as follows:

1. **By fusion:** Brass (90% Cu + 10% Zn) and bronze (90% Cu + 10% Sn) are prepared by this method.
2. **By reduction:** Aluminium bronze is prepared by heating aluminium oxide and carbon in presence of the required amount of Cu.

$$Al_2O_3 + 3C + Cu \rightarrow (Al + Cu) + CO\uparrow$$

3. **By compression:** The required metals are first converted into thin sheets and then rolled together and hammered under high pressure to give the alloy. Alloys like solder (50% Pb + 50% Sn) are prepared by this method.
4. **By simultaneous electrodepositon:** An aqueous solution of the salts of the component metals is taken in an electrolytic cell and electric current is passed. The desired metals are deposited simultaneously on the cathode to give the desired alloy. For example, brass is obtained by electrolysis of a solution containing Cu and Zn cyanides in KCN solution.

Some important alloys with their compositions and uses are listed in Table 6.2.

Table 6.2 Composition and uses of some important alloys

	Alloy	Composition	Products manufactured
1	Magnelium	Al : 98%, Mg : 2%	Balances
2	Duralumin	Al : 95%, Cu : 4% Mg : 0.5%, Mn : 0.5%	Air craft parts, boat machinery
3	Aluminium bronze	Al : 10%, Cu : 90%	Coins, photo frames, utensils, golden paints
4	Alnico	Al : 20%, Ni : 20% Co : 10%, Steel : 50%	Permanent magnets
5	γ-Alloy	Al : 92%, Cu : 4% Mg : 1.5%, Ni : 2.5%	Pistons and machine parts
6	Nickeloy	Al : 95%, Cu : 2%, Ni : 1%	Aircraft parts
7	Pewter	Pb : 20, Sn : 50	Utensils
8	Solder	Pb : 75, Sn : 80	Soldering
9	Type metal	Pb : 20, Sn : 5, Sb : 20	Printing type

(continued)

Table 6.2 (continued)

	Alloy	Composition	Products manufactured
10	Bell metal	Cu : 80, Sn : 20	Bells making
11	Babbit metal	Sn : 90, Sb : 7, Cu : 3	Bearing of machinery
12	Frary metal	Pb : 97%, Ba : 2%, Ca : 1%	Bearing of machine
13	Lino type metal	Pb : 83%, Sn : 3%, Sb : 14%	Printing type
14	Brass	Cu : 70%, Zn : 30%	Utensils
15	Bronze	Cu : 88-96%, Sn : 4-12%	Utensils, coins, statues
16	Monel metal	Cu : 27%, Ni : 68%, Fe : 5%	Pumps, turbines of ships, boilers
17	German silver	Cu : 50%, Zn : 30%, Ni : 20%	Flower vases and ornaments
18	Electron	Mg : 95%, Zn : 4.5, Cu : 0.5%	Parts of aeroplane and motor cars
19	Dutch metal	Cu : 80%, Zn : 20%	Golden yellow colour used for decorative purpose
20	Nichrome	Ni, Cr, Fe	
21	Gun metal	Cu : 87%, Zn : 3%, Sn : 10%	
22	Con Stantan	Cu : 60%, Ni : 40%	
23	Artificial gold	Cu : 90%, Al : 10%	
24	14 Carat gold	Au : 54%, Ag : 14% to 30%, Cu : 12-28%	
25	24 Carat gold	100% Au	
	Alloys of steel		
1	Vanadium	V : 0.2-1%	
2	Chromium	Cr : 2-4%	
3	Nickel	Ni : 3-5%	
4	Manganese steel	Mn : 10-18%	
5	Stainless steel	Cr : 12-14% and Ni : 2-4%	
6	Tungston	W : 10-20%	
7	Invar	Ni : 36%	

Amalgam

Treating different metals like Sn, Zn, Au, Na, Ag, etc. with mercury produces amalgams. Some uses of amalgam are

1. Ag–Hg or Au–Hg amalgams are used in filling dental cavities.
2. Tin amalgam is used for silvering mirrors.
3. Na–Hg amalgam is utilized to have decreased reactivity of Na.

6.9 | DIFFERENT TYPES OF FURNACES USED IN METALLURGY

Various types of furnaces used in metallurgical processes are listed below:

1. **Blast furnace:** Mainly the smelting of the roasted ore is carried out in this furnace (discussed under extraction of Fe).
2. **Reverberatory furnace:** Mainly roasting and calcination are done in this kind of furnace (Figure 6.15).

3. **Muffle furnace:** It is basically a closed chamber which is heated using an external heating arrangement so that the material to be heated does not come in direct contact with the fuel. This is used in small-scale metallurgical processes.
4. **Electric furnace:** This is used where very high temperature is necessary and the high temperature is achieved by an electric arc struck between two graphite electrodes.

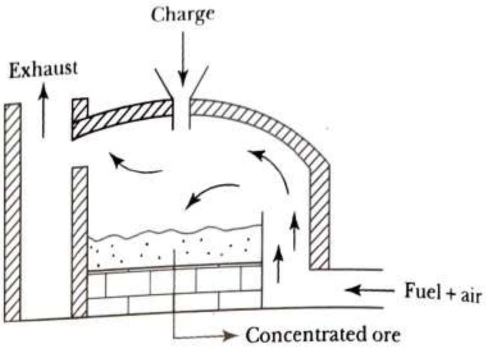


Figure 6.15 Reverberatory furnace.

6.10 | EXTRACTION OF SILVER

Important ores of silver are

1. Argentite or silver glance : Ag_2S
2. Ruby silver : $3Ag_2S \cdot Sb_2S_3$
3. Stromeyerite or silver copper glance : $Ag_2S \cdot Cu_2S$
4. Horn silver : AgCl

There are three processes commonly used for extraction of Ag. The cyanide process is described below. The other two processes, i.e. Parke's process and Pattinson's process are beyond the scope of discussion.

Cyanide process or Mc-Arthur Forest Process: This process is depicted in the flow diagram given in Figure 6.16.

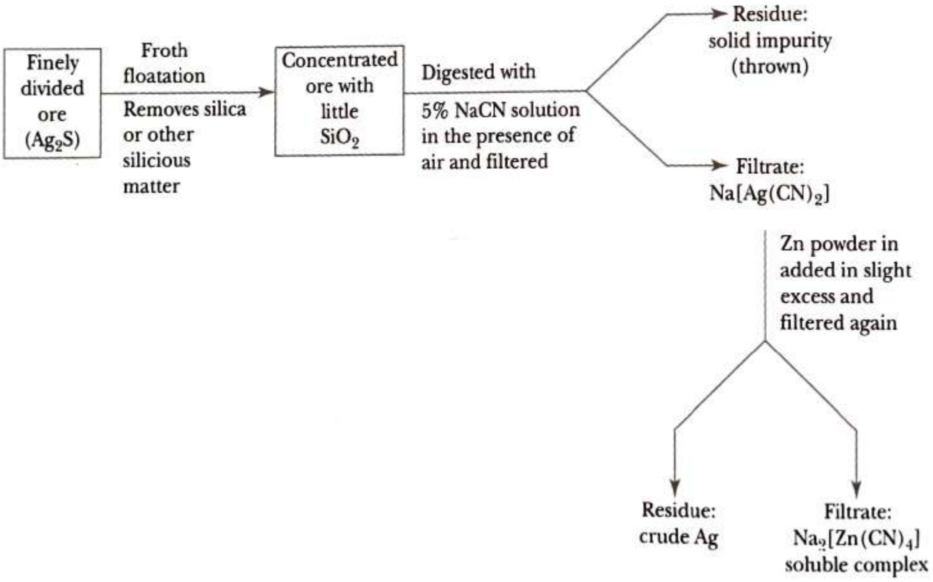


Figure 6.16 Flow chart for Mc-Arthur Forest process for extraction of silver.

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

1. $Ag_2S + 4NaCN(excess) \rightleftharpoons 2[Ag(CN)_2]^- + Na_2S + 2Na^+$

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

   Since the above reaction is reversible, the conversion ratio is not good. Hence the process is carried out in the presence of air which converts the Na_2S produced into Na_2SO_4 and S and the overall reaction becomes unidirectional.

2. In the step involving precipitation of Ag, a little excess of Zn powder is added by which $Na[Ag(CN)_2]$ becomes the limiting reagent, otherwise the loss of Ag will be more. Here Zn is chosen because it is more electropositive as compared to Ag and the replacement reaction occurs very easily.

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

Refining of Ag

Refining of silver is carried by electrolytic process.

$$\underset{\begin{pmatrix}\text{Zn, Cu, Au}\\ \text{as impurity}\end{pmatrix}}{\text{Crude Ag}} \xrightarrow[\text{(Mobius process)}]{\text{electrolytic refining}} \underset{\begin{pmatrix}\text{upto } 99.6-99.9\%\\ \text{pure Ag}\end{pmatrix}}{\text{Pure Ag}}$$

Electrolyte : $AgNO_3$ solution + 10% HNO_3
Cathode : Pure Ag strip
Anode : Impure Ag slab

Reactions at the electrodes:
At cathode : $Ag^+ + e \rightarrow Ag$
At anode : $Ag \rightarrow Ag^+ + e$

6.11 | EXTRACTION OF GOLD BY CYANIDE PROCESS

The flow diagram for different stages involved in the cyanide process for extraction of gold is shown in Figure 6.17.

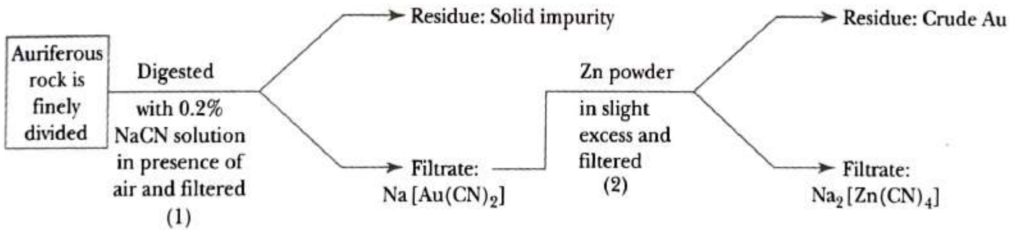


Figure 6.17 Flow chart for cyanide process for extraction of gold.

Reactions taking place in different steps are:

1. **In step 1:**

$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

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

2. **In step 2:**

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

Refining of Au

The steps involved in the refining of Au are given in Figure 6.18. In the third step, on heating with borax, the soluble metaborate of Cu, i.e. $Cu(BO_2)_2$, is formed and washed out with water. Similarly, in the fourth step also Ag dissolves out as Ag_2SO_4 leaving behind pure Au.

Note: 1. The removal of Ag can also be carried out using chlorine or by electrolysis.
2. Cupellation is a process, where crude gold is taken in a small bowl called cupell and melted in the presence of air. Due to high oxygen affinity of Pb, it is converted into PbO (volatile) and escapes from the system.

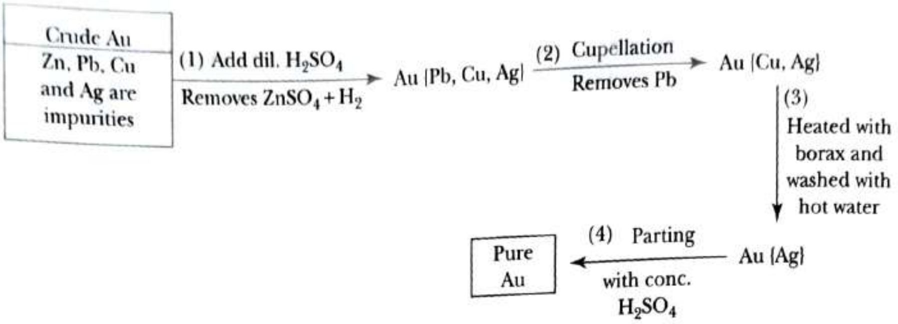


Figure 6.18 Flow chart for refining of gold.

6.12 | EXTRACTION OF TIN

An important ore of tin is cassiterite or tin stone (1–5% SnO_2 present in it). The main impurities present in the ore are sand (SiO_2), pyrite of Cu and Fe, and wolframite [$FeWO_4 + MnWO_4$]. The flow chart for extraction of Sn is depicted in flow chart in Figure 6.19.

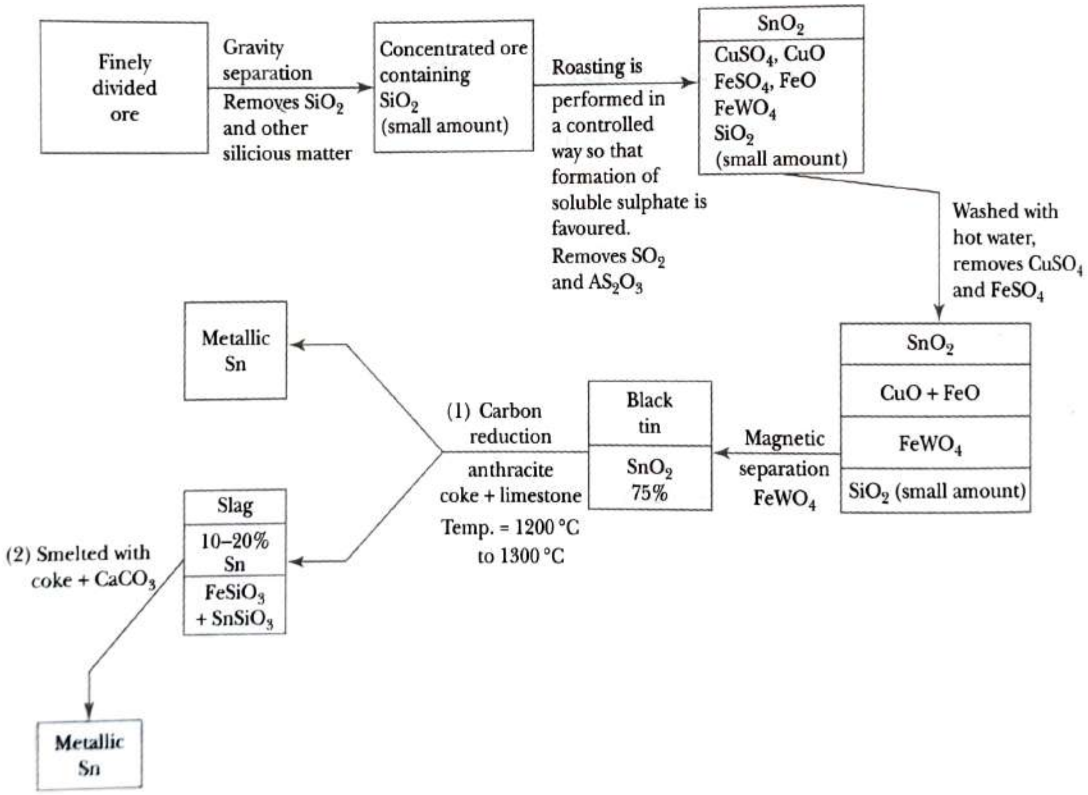


Figure 6.19 Flow chart for extraction of tin.

The reactions taking place in the extraction of Sn are:

1. **In step 1:**

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

2. **In step 2:**

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