METALLURGY

Various steps of metallurgy are :

1. **Concentration of ore – Crushing**
   - (*i*) Levigation – washing
   - (*ii*) Magnetic separation
   - (*iii*) Froth floatation process
   - (*iv*) Leaching
2. **Conversion of metal into metal oxide**
   - (*i*) Calcination
   - (*ii*) Roasting
3. **Reduction of metal oxides to free metal**
   - (*i*) Smelting
   - (*ii*) Reduction with CO
   - (*iii*) Reduction with highly electropositive metal
   - (*iv*) Reduction with H_2
   - (*v*) Self reduction
   - (*vi*) Reduction by electrolysis

4. Refining or purification of metal

(*i*) Liquation

(*ii*) Distillation

(*iii*) Zone refining

(*iv*) Park's distribution process

(*v*) Cupellation

(*vi*) Poling

(*vii*) Electrolytic refining

(*viii*) Van Arkel process

5. Occurrence of elements

(*i*) ***Elements in atmosphere*:** The atmosphere mainly contains nitrogen (78.09%), oxygen (20.95%) and other geses (about 1%)

(*ii*) ***Elements in sea*:** Sea is the source of elements like Br, I, Ni, Cu, Zn, Sn, Au etc.

(*iii*) ***Elements in earth crust (lithosphere)*:** Elements occur in two states:

(*a*) ***Free or native state*:** Less reactive metals like copper, silver, gold, platinum etc. occur in free state. These metals are generally

associated with rocky meterials, sand, clay etc. known as **gangue** or **matrix**.

(*b*) ***Combined state (minerals)*:** Reactive metals occur in combined state known as **minerals**. Those minerals from which metal can be profitable extracted are called as **ores**.

6. Classification of ores of elements

(*a*) ***Free or native ores*:** Copper, silver, gold and platinum exist in free state.

(*b*) ***Oxide ores*:** Bauxite ($Al_2O_3.2H_2O$) of aluminium, haematite (Fe_2O_3) of iron, zincite (ZnO) of zinc, pyrolussite (MnO_2) of manganese are main oxide ores.

(*c*) ***Halide ores*:** Carnallite (KCl. $MgCl_2$. $6H_2O$) of potassium, rock salt (NaCl) of sodium, cryolite (Na_3AlF_6) of aluminium are main halide ores.

(*d*) ***Carbonate ores*:** Calcite ($CaCO_3$) of calcium, dolomite ($MgCO_3$. $CaCO_3$) of magnesium, malachite [$CuCO_3$. $Cu(OH)_2$] of copper are main carbonate ores.

(e) ***Sulphide ores*:** Iron pyrites (FeS_2) of iron, galena (PbS) of lead, copper pyrites (CuS. FeS) of copper, cinnabar (HgS) of mercury, zinc blende (ZnS) of zinc are main sulphide ores.

(f) ***Sulphate ores*:** Barytes ($BaSO_4$) of barium, alglesite ($PbSO_4$) of lead are main sulphate ores.

(g) ***Silicate ores*:** Silicon does not occur in free state but is commonly found combined with oxygen, called as silicates. Many elements like, Fe, Mg, K, Na, Ca, Al are found combined with silicates.

Extraction of metals

1. **Concentration of ore:** Concentration of ore provides removal of unwanted substances.

   I. **Crushing of ore:** Big lumps of ore obtained from earth crust are crushed into smaller pieces with the help of jaw crushers and grinders. This process is called as crushing of ore.

II. Removal of impurities from the crushed ore

(*a*) *Hand picking*: Selected pieces of ores are picked up.

(*b*) *Levigation-washing*: The crushed ore is washed in a stream of water. The lighter impurities are swept away but heavier ore particles settle down. Iron ores and tin ores are concentrated by this method.

(*c*) *Froth floatation process*: This process is commonly used for sulphide ores and is based upon different wetting characteristics of ore and gangue particles. Finely powdered ore is mixed with water, pine oil and ethylxanthate or potassium ethyl xanthate in a big tank. The whole mixture is agitate with air. The ore particles wetted with oil come in froth, are taken off but impurities wetted with water settle at the bottom.

(*d*) *Magnetic separation*: In this method powdered ore is placed

over leather belt which moves over two rollers one of which is magnetic. If the crushed ore is passed over magnetic roller, magnetic ore particles are attracted by it and fall below it while impurities fall away from the magnetic roller. Rutile (TiO_2) from apatite, chromite [$Fe(CrO_2)$] from silicious, and wolframite ($FeWO_4$) from cassiterite are separated by this method.

(e) ***Leaching*:** In this method powdered ore is treated with a suitable chemical reagent that dissolves the ore while impurities remain insoluble in that reagent.

2. Conversion of metal into metal oxide

(a) Calcination: It is the process of heating ore below their melting point in absnece of air to remove volatile impurities like water, CO_2 etc. and organic matter etc.

$$\underset{\text{Lime stone}}{CaCO_3} \rightarrow CaO + CO_2\uparrow$$

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \rightarrow \underset{\text{Alumina}}{Al_2O_3} + 2H_2O\uparrow$$

(b) Roasting: It is the process of heating ore in excess of air so that metals convert into their oxides and water insoluble sulphides to water soluble sulphates.

$$\underset{\text{Pyrite}}{2FeS} + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2$$

$$\underset{\text{Cinnabar}}{2HgS} + 3O_2 \xrightarrow{\Delta} 2HgO + 2SO_2$$

$$\underset{\text{Lead sulphide}}{PbS} + 2O_2 \xrightarrow{\Delta} PbSO_2$$

$$\underset{\text{Zinc sulphide}}{ZnS} + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

3. Reduction of metal oxides of free metal

(a) Reduction with carbon (smelting): Reduction of oxides of less electropositive metals like Fe, Pb, Sb, Zn and Cu is carried out by heating them with coal or coke.

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Coke}}{C} \xrightarrow{\Delta} Zn + CO$$

$$\underset{\text{Lead monoxide}}{PbO} + \underset{\text{Coke}}{C} \xrightarrow{\Delta} Pb + CO$$

Flux is a substance added to remove non-fusible impurities from roasted or calcined ore as fusible substance called as **slag**.

Flux + non-fusible impurity → Fusible slag

Acid flux is used to remove basic impurties like silica (SiO_2)

$$\underset{\substack{\text{Ferric oxide}\\\text{(basic impurity)}}}{Fe_2O_3} + \underset{\substack{\text{Silica}\\\text{(acid flux)}}}{3SiO_2} \rightarrow \underset{\substack{\text{Ferric silicate}\\\text{(slage)}}}{Fe_2(SiO_3)_3}$$

Basic flux is used to remove acidic impurties, like calcium oxide (CaO).

$$\underset{\substack{\text{Phosphours pentoxide}\\\text{(Acidic impurity)}}}{P_2O_5} + \underset{\substack{\text{Calcium oxide}\\\text{(basic flux)}}}{3CaO} \rightarrow \underset{\substack{\text{Calcium phosphate}\\\text{(slag)}}}{Ca_3(PO_4)_2}$$

(*b*) Reduction with carbon monoxide: CO produced by heating coke in limited supply of oxygen, is also used as reducing agent.

$$\underset{\text{Ferric oxide}}{Fe_2O_3} + 2CO \rightarrow 2Fe + 3CO_2$$

$$\underset{\text{Lead monoxide}}{PbO} + \underset{\text{Carbon monoxide}}{CO} \rightarrow \underset{\text{Lead}}{Pb} + \underset{\text{Carbon doxide}}{CO_2}$$

(c) Reduction with highly electropositive metal: Some metal oxides which are not reduced by carbon, such as titanium chloride ($TiCl_4$), chromium trioxide (Cr_2O_3), manganese oxide (Mn_3O_4) are reduced by using Al, Mg etc.

$$\underset{\text{Manganese oxide}}{3Mn_3O_4} + 8Al \rightarrow 9Mn + \underset{\text{Aluminum oxide}}{4Al_2O_3} + Heat$$

$$\underset{\text{Chromium trioxide}}{Cr_2O_3} + 2Al \rightarrow 2Cr + \underset{\text{Aluminium oxide}}{Al_2O_3} + Heat$$

$$\underset{\text{Titanium trioxide}}{TiCl_4} + 2Mg \xrightarrow{\Delta} \underset{\text{titanium}}{Ti} + \underset{\text{Magnesium chloride}}{3MgCl_2}$$

(d) Reduction with hydrogen:

$$\underset{\text{Tungsten trioxide}}{WO_3} + 3H_2 \xrightarrow{\Delta} \underset{\text{Tungsten}}{W} + 3H_2O$$

$$\underset{\text{Molybdenum trioxide}}{MoO_3} + 3H_2 \rightarrow \underset{\text{Molybdenum}}{Mo} + 3H_2O$$

(e) Self reduction: Sulphide ores of less electropositive metals such as Hg, Cu, Pb, Sb etc. undergo self reduction.

$$\underset{\text{Mercury (II) oxide}}{2HgO} + \underset{\text{Mercury (II) sulphide}}{HgS} \rightarrow 3Hg + SO_2$$

$$\underset{\text{Cinabar}}{2HgS} + 3O_2 \rightarrow \underset{\text{Mercury (II) oxide}}{2HgO} + 2SO_2$$

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

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

(f) Reduction by electrolysis: Alkali and alkaline metals are extracted by this method. Such as sodium metals is obtained by the electrolysis of fused sodium chloride.

$$NaCl \rightarrow Na^+ + Cl^-$$

At cathode: $Na^+ + e^- \rightarrow Na$

At anode : $Cl^- - e^- \rightarrow Cl$

$$Cl + Cl \rightarrow Cl_2$$

Some Important Facts

I. Alkali and alkaline earth metals being good reducing agents cannot be prepared by reduction of their oxides.

II. Alkali metals are highly electropositive, so also cannot be prepared by displacing them from their salts.

III. Alkali metals dissolve in ammonia to form blue solution which is good conductor of electricity due to presence of solvated electrons.

IV. KOH is a better absorber of CO_2 than NaOH.

V. Sodium hydroxide is called as caustic soda because it breaks down the protein of skin to a pasty mass.

VI. Gypsum is added to cement to prolong its setting time.

VII. Magnesia cement is the saturated solution of magnesium chloride and magnesium oxide ($MgCl_2 . 5MgO . xH_2O$).

VIII. Thomas slag formed in Bessemer process is used as fertilizer.

IX. Zinc atom is larger than copper atom, because it has fully filled d-orbitals.

X. Hardness of steel increases with increase in carbon content.
