METALLURGY

The branch of chemistry which deals with the methods of extraction of metals from their ores and alloy formation, is called metallurgy.

Modes of Occurrence of Elements

Element may occur either in the native (or free) state or int he combined state. This is mainly due to the reason that different elements possess different chemical reactivities.

(i) Native State : Element which are not attacked by moisture,oxygen and carbon dioxide of the air occur in the native state. For example, gold, platinum, noble gases etc.

(ii) Combined state : Elements which are readily attacked by moisture, oxygen and carbon dioxide of the air occur in the combined state in form of their compounds called minerals. In the combined state non-metals are found in the reduced from while metals are found in the oxidised from such as elements are generally present as oxides, Carbonates, sulphides, silicates etc. as shown is table.

Ore Type	Examples
Native	Cu, Ag, Au, Hg, As, Bi, Sb, Pd, Pt, S, noble gases
Oxides	$Al2O_3.\ H_2O$ (diaspore) $Al_2O_3.\ 2H_2O$ (bauxite), MnO_2 (pyrolusite),
Carbonates	$CaCO_3$ (calcite), $CaCO_3.\ MgCO_3$ (dolomite), $FeCO_3$(siderite).
Sulphides	Ag_2S (silver glance or argentite), Cu_2S (copper glance or chalacocite), copper pyrites ($CuFeS_2$), PbS (lead glance), ZnS (zinc blende).
Halides	AgCl (silver glance)
Sulphates	$BaSO_4$, $CaSO_4.2H_2O$

Composition of earth's crust :

Earth's crust is the main source of elements. Oxygen is the most abundant non-metal and aluminium is the most abundant metal in the earth's crust.

Minerals :

The various compounds of metals which occur in the earth's crust and are obtained by mining, are called minerals. A mineral may be a single compound or a mixture.

Ore :

The mineral from which a metal can be profitably and easily extracted is called an ore.

All ores are minerals but all the minerals are not ores.

Gangue or Matrix :

The undesirable impurities (clay, sand, pebbles, etc.) present in an ore are called gangue or matrix.

Flux : Flux is an external material that is added during smelting to convert infusible impurities into an easily fusible material known as slag.

$$\text{Flux + Infusible gangue} \rightarrow \text{Slag.}$$

Acidic flux : It is used to remove basic impurities. The cheapest acidic flux is SiO_2 (silica).

Acidic flux + basic gangue $\rightarrow$ slag.

Basic flux : It is used for removing acidic impurities. Examples are CaO, MgO, etc.

Basic flux + acidic gangue $\rightarrow$ slag.

Slag : It is the product of the reaction between flux and infusible impurities. Slag possesses following properties.

(a) Molten slag is not miscible with molten metal.

(b) Melting poing of slag is lower than that of the metal.

(c) Density of molten slag is lower than that of molten metal and hence molten slag floats over molten metal.

Refractory material is that substance which can withstand a very high temperature without getting decomposed or becoming soft. The refractory material may be acidic (Silica, Quartz, sandstone etc.), basic (lime, dolomite, magnesite) and neutral (Graphite, Chromite, bone ash etc.)

EXTRACTION OF METALS :

The extraction of a metal from its ore is completed in the following four steps.

A. Concentration of the ore

B. Calcination and Roasting

C. Reduction to the metal

D. Refining of the metal

A. Concentration, Beneficiation or ore dressing :

The removal of impurities from the ore is called its concentration. It is carried out in one or more of the following ways :

(i) Gravity separation or Levigation : This method of concentration of the ore is based on the difference in the specific gravities of the ore and the gangue particles. Powdered ore is agitated with a running stream of water. The lighter gangue particles are taken away by water while heavier ore particles settle down.

(ii) Froth Floatation method : This method is mainly employed for the concentration of sulphide ores. The method is based on the different wetting characteristics of the gangue and the sulphide ore with water and oil. The gangue is preferrentially wetted by water and the ore by oil.

The crushed ore along with water (slurry) is taken in a floatation cell. Various substances (additives) are added depending on the nature of the ore and a current of air is blown in. The substances added are usually of three types :

(a) Frothers : They generate a stable froth which rises to the top of the tank. The best example of frother is pine oil. Other oils such as eucalyptus oil, creosote oil, etc. may also be used.

Froth is a colloidal system of gas in liquid. It has very good adsorption capacity.

(b) Collectors : Ethyl xanthate and Potassium Ethyl Xanthate are used as collectors. These attach themselves by polar groups to the grains of the ores which then become water repellant and pass on into the froth.

(c) Activators or depressants : These reagents activate or depress the floatation properly and help in the separation of different sulphide ores present in a mixture. An example of a depressant is NaCN and alkali. An activator is $CuSO_4$.

(iii) Magnetic separation :

(iv) Chemical separation : Some of the ores are concentrated by means of chemical treatment. For example, bauxite ($Al_2O_3.2H_2O$) associated with the oxides of iron, titanium, and silicon, is purified by this method.

Leaching : It involues the treatment of the ore with a suitable reagent which dissolves the ore while impurities are left insoluble. It is used for concentration of Au and Ag ores by dissolving them as their cyanide complexes. Also is Boeyer's process for concenteration of Bauxite containing Fe_2O_3 as impurity, Al_2O_3 is leached out with NaOH sol in the form of sodium meta aluminate.

B. Calcination :

It is the heat treatment given to oxide, hydroxide or carbonate ores. The concentrated ore is heated in a reverberatory furnace, below its melting point, in the limited supply of air without addition of any external substance.

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow[\Delta]{\text{Calcination}} ZnO + CO_2$$

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow[\Delta]{} 2CuO + CO_2 + H_2O$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$$

Advantages of Calcination :

(i) Moisture is removed

(ii) Organic matter is destroyed

(iii) The hydroxide and the carbonate ores are converted into their oxides

(iv) The mass becomes porous and easily workable.

Roasting : The removal of excess sulphur contained in sulphide ores by heating in an excess of air is called roasting.

Advantages of Roasting :

(i) Excess of sulphur is removed as volatile oxide.

$$S + \underset{(air)}{O_2} \rightarrow SO_2 \uparrow$$

(ii) Impurities of arsenic and antimony are removed as their volatile oxides.

$$4As + \underset{(air)}{3O_2} \xrightarrow{\Delta} 2As_2O_3 \uparrow$$

$$4Sb + 3O_2 \xrightarrow{\Delta} 2Sb_2O_3 \uparrow$$

(iii) The metal sulphide is converted into metal oxide.

Roasting of Galena ; zinc blende, etc.

$$\underset{\text{Galena}}{2PbS} + \underset{(air)}{3O_2} \xrightarrow{\text{Roasting}} 2PbO + 2SO_2 \uparrow$$

$$\underset{\text{Zinc}}{2ZnS} + \underset{\text{blende}}{3O_2} \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2 \uparrow$$

Roasting of copper pyrites :

$$2CuFeS_2 + \underset{(air)}{O_2} \xrightarrow{\text{Roasting}} Cu_2S + 2FeS + SO_2 \uparrow$$

$$2Cu_2S + \underset{(air)}{3O_2} \rightarrow 2Cu_2O + 2SO_2 \uparrow$$

$$2FeS + \underset{(air)}{3O_2} \rightarrow 2FeO + 2SO_2 \uparrow$$

C. Reduction to the Metal :

The compound of the metal obtained after calcination and roasting of the ore is reduced to get the metal. Depending upon the nature of the metal, the following methods of reduction are used :

(i) Cathodic or Electrolytic reduction : This method is mainly used in the extraction of highly electropositive metals. For example, alkali metals (IA), alkaline earth metals (IIA), lanthanides, and aluminium.

Except aluminium, all the other metals are prepared by the electrolysis of their fused salts (particularly the chlorides).

(ii) Chemical reduction (Smelting) : In this method, chemical substances such as active metals, carbon (coke), etc., are used as reducing agent to prepare less active metals such as chromium, manganese, nickel, tin, etc.

Smelting : The process which involves melting in the extraction of metal from its ore, is called smelting.

(a) Active metals as reducing agents :

Na, Mg, Al, Ca, etc., metals are used as reducing agents in the preparation of less active metals :

For example : Titanium and Zirconium are obtained as follows :

$$\underset{\text{Rutile}}{TiO_2} + 2C + 2Cl_2 \xrightarrow{\Delta} TiCl_4 + 2CO\uparrow$$

$$TiCl_4 + 4Na \xrightarrow[\text{Kroll's process}]{\Delta,\text{Ar}} Ti + 4NaCl$$

Goldschmidt thermite process : In this process, metallic aluminium is used as a reducing agent. Chromium and manganese are obtained by the reduction of their oxides by aluminium.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 3Cr + \text{heat}$$

$$3MnO_2 + 4Al \xrightarrow{\Delta} 2Al_2O_3 + 3Mn + \text{heat}$$

(b) Carbon as reducing agent : Carbon, often in the form of coke, is used as a reducing agent for metal oxides.

$$\text{Metal oxide} + \underset{\text{coke}}{C} + \text{flux} \xrightarrow{\text{smelting}} \text{Metal} + CO\uparrow + \text{slag}$$

Carbon reduction for tin : Calcined cassiterite is mixed with carbon (anthracite coal) and lime (CaO) and heated to melt.

$$SnO_2 + 2C + \underset{\text{basic flux}}{CaO} \xrightarrow{\text{Smelting}} Sn + 2CO + \text{slag}$$

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

Carbon reduction for Zn :

$$\underset{\text{Zinc blende}}{2ZnS} + \underset{\text{(air)}}{3O_2} \xrightarrow[\text{Re verberatory furnace}]{\text{Roasting in}} \underset{\text{Zinc oxide}}{2ZnO} + 2SO_2\uparrow$$

$$\underset{\text{Roasted ore}}{ZnO} + \underset{\text{Coke}}{C} \xrightarrow[\text{strongly}]{\text{heated}} Zn + CO\uparrow$$

(c) Carbon monoxide as reducing agent

$$3Fe_2O_3 + CO \xrightarrow{500°C} 2Fe_3O_4 + CO_2\uparrow$$

$$Fe_3O_4 + CO \xrightarrow{600°C} 3FeO + CO_2\uparrow$$

$$FeO + CO \xrightarrow[\text{Spongy iron}]{700°C} Fe + CO_2\uparrow$$

D. Refining of Metals :

Metal obtained by the reduction of its compound still contains some objectionable substance and has to be refined. Depending upon the nature of the metal and impurities, the following methods are used for purification of metals :

(i) Liquation : This method is used for the refining of metals having low melting point and are associated with high melting impurities. Examples, Pb, Sn, Sb and Bi. The impure metal is heated on the sloping hearth of a furnace. The pure metal flows down leaving behind the non-fusible material on the hearth.

* The infusible matter during liquation is called dross.

(ii) Zone refining : Metals of very high purity are obtained by zone refining. This refining method is based on the fact that impurities tend to remain dissolved in molten metal. Ge, Si and Ga, used as semiconductor are refined in this manner.

(iii) Oxidation processes : These processes are used for refining of metals associated with impurities having high affinity for oxygen than the metal itself. Cupellation and bassemerization are important oxidation processes employed for refining different metals.

* Cupellation is used for the purification of silver associated with lead as impurity.

(iv) Vapour phase refining : In this method, metal is removed as a volatile compound from impure metal sample. This volatile compound is decomposed on heating to give pure metal. For example,

(a) Mond's process : This method is used for the purification of nickel.

Ni forms a volatile carbonyl compound at 25°—50°C which decomposes at about 180°C.

$$Ni(s) + 4CO(g) \xrightarrow{25°C—50°C} \underset{\text{Nickel tetra carbonyl, volatile compound}}{Ni(CO)_4(l)}$$

$$Ni(CO)_4(g) \xrightarrow{180°C} \underset{\text{pure}}{Ni(s)} + 4CO(g)$$

(b) Van-Arkel process : Ti, Zr, Hf, Si, U are refined by this process. For example, impure Zr is heated with a limited amount of I_2 in an evacuated glass apparatus at 523 K. The vapours of ZrI_4 formed are allowed to diffuse on a tungston filament heated at about 1800K. The gas zirconium tetraiodide is decomposed on coming in contact with hot filament and pure metal is deposited on it.

$$\underset{\text{Impure}}{Zr(s)} + 2I_2(g) \rightarrow ZrI_4(g)$$

$$ZrI_4(g) \xrightarrow[\text{W-filament}]{\approx 1800\,K} \underset{\text{pure}}{Zr(s)} + 2I_2$$

(v) Electro-refining of metals : Metals such as Cu, Ag, Zn, Sn, Pb, Al, Ni, Cr, are refined by this method. The impure metal is made the anode of an electrolytic cell, while catho9de is a thin plate or pure metal. Electrolyte is the solution of a soluble salt of the metal. On passing the electric current, pure metal from the anode dissolves and gets deposited at the cathode. The soluble impurities go into the solution while insoluble impurities settle down below the anode as anode mud or sludge.

e.g.

(a) Electro refining of Copper
Anode : Blister copper (98% purity).
Cathode : Pure copper.
Electrolyte : An aqueous solution of $CuSO_4$ (15%) + (5%) dil. H_2SO_4.

(vi) Cupellation : The impurity of Pb present in Ag is removed by cupellation. The cupel is a boat shaped dish made up of bone ash or cement. The crude metal is taken in the cupel and blast of hot air is blown over it. The impurities escape is the form of volatile oxides leaving behind the pure metal, e.g., Pb impurity is converted into litharge (PbO) which being volatile escapes leaving behind pure silver.