General Principles & Processes of Isolation of Elements

METALLURGY

The science and technology of isolation of pure metals from their ores and preparing them for practical use. The process includes-

- Mining - getting the ore out of ground
- Concentration - preparing for further treatment
- Reduction - to obtain the metals in zero oxidation state
- Refining - to obtain the pure metal
- Mixing with other metals - to form an alloy

Minerals

Most metals are found in nature in the form of solid inorganic compounds called minerals. Names of minerals are based on the location of their discovery, the person who discovered them or some characteristics of the mineral.

Ore

The mineral from which the metal can be extracted economically. Hence all minerals cannot be classified as ores. The most important ores are oxide, sulphide and carbonate minerals.

Gangue or Matrix

The unwanted rocky, earthy or sandy materials almost always associated with the ores as impurities are called gangue or matrix.

Flux and Slag

Flux is a substance added to the ores before heating which combines chemically with earthy impurities (gangue) and form a fusible mass known as slag.

Flux can be **Acidic** e.g.SiO_2 (silica), $Na_2B_4O_7.10H_2O$ (borax); **Basic** e.g. CaO, MgO; or **Neutral** - neutral compounds, and they decrease the melting point and make the order conducting in an electrolytic cell e.g. CaF_2, Na_3AlF_6, KF etc.

Slag consists mostly of molten silicates, aluminates, phosphates, fluorides and other inorganic materials. The formation of slag is known as **slagging**.

Concentration or Dressing

The process of the removal of gangue or matrix from the ore is known as concentration. It is achieved by-

- Hand picking
- Gravity separation (hydraulic-washing)
- Magnetic separation
- Electrostatic separation
- Froth flotation process -for sulphide ores.
- Leaching

Froth flotation process - Finely divided ore is mixed with oil (pine oil, eucalyptus oil or camphor oil) and agitated with water containing a detergent (foaming agent). When air is bubbled through the mixture, the air bubbles are stabilised by the detergent. These adsorb mineral particles wetted with oil and rise to the surface. The earthy matter wetted by water settles down at the bottom.

Collectors - Which increase the non wettability of ore particles e.g. pine oil, xanthates and fatty acids.

Froth stabilizers - Which stabilise the froth e.g. cresoles and aniline.

Depressants - Depressants prevent the formation of froth e.g. NaCN, when added to ore containing ZnS and PbS form a complex with ZnS as $Na_2[Zn(CN)_4]$ and prevent it from forming froth. PbS is then easily separated from ZnS.

Leaching - Leaching is the selective dissolution of the desired mineral leaving behind the impurities in a suitable dissolving agent e.g. bauxite when treated with strong solution of NaOH, dissolves leaving behind $Fe_2O_3.SiO_2$..

$$Al_2O_3 + 6NaOH \rightarrow 2NaAlO_3 + 3H_2O$$

$$Na_3AlO_3 + 3H_2O \rightarrow 3NaOH + Al(OH)_3$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Leaching is also employed in Ag ore and native gold.

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + NaS$$

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

$$4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$$

Calcination

It is the heating of the ore in a suitable furnace in absence of air much below its melting point to cause decomposition and elimination of volatile products.

$$PbCO_3 \rightarrow PbO + CO_2$$

The process is generally applied to hydrated oxide or carbonate ores.

Roasting

It is the heating of the concentrated ore in a suitable furnace strongly in presence of air with or without certain substances below the melting point which causes chemical reaction to expel volatile impurities e.g. oxides of S, As and Sb.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2MoS_2 + 7O_2 \longrightarrow 2MoO_3 + 4SO_2$$

Reduction

After calcination or roasting, the metal oxides are reduced and impurities are removed as slag. Reduction and slagging take place together.

Removal of Impurities as Slag

For acidic impurities viz. basic flux is added.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

For basic impurities like MnO acidic flux is added.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

Reduction of Oxides

Decomposition of Oxides by Heating

For thermally unstable oxide.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

Hg is obtained from its sulphide ore cinnabar directly in the roasting step.

Reduction by Carbon

Sn from oxide ore cassiterite SnO_2 is obtained by heating with coke.

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

Zn from sulphide ore Zinc blende (ZnS).

$$2ZnS + 3O_2 \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2$$

$$ZnO + C \longrightarrow Zn + CO$$

Iron is obtained from oxide ore haematite (Fe_2O_3).

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

Reduction by H_2 and CO

$$MoO_3 + 3H_2 \longrightarrow MO + 3H_2O$$

$$CuO + CO \longrightarrow Cu + CO_2$$

Reduction by Other Metals

e.g. Al and Mg

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

$$Rb_2O_3 + 3Mg \longrightarrow 3MgO + 2Rb$$

Self Reduction

Cu, Pb and Mg are obtained by self reduction in roasting.

$$Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$$

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

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

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

Electrolytic Reduction

Oxides of very active metals like alkali or alkaline earth is not easily reduced by chemical reducing agents e.g. Na, Mg, and Al etc. They are obtained by electrolytic reduction.

$$2NaCl \xrightarrow{\text{Fusion}} 2Na^+ + 2Cl^-$$

At anode : $2Cl^- - 2e^- \rightarrow Cl_2$

At cathode: $2Na^+ + 2e^- \longrightarrow 2Na$

Amalgamation Process

Ag and Au are obtained by leaching process using solution of KCN or NaCN to form argento cyanide or aurocyanide . Ag and Au is precipitated by adding Zn dust.

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

$$2K[Au(CN)_2] + Zn \longrightarrow \underset{\text{Soluble complex}}{K_2[Zn(CN)_4]} + 2Au$$

Refining

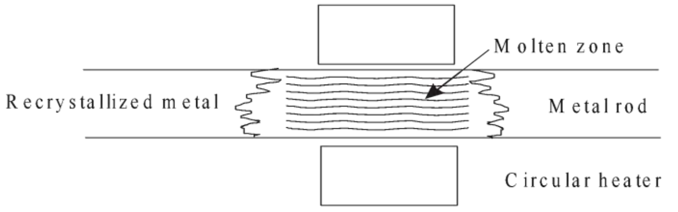
The methods employed for the refining of metals are-

Liquation

Impurities present must be less fusible than the metal to be purified. Impure metal is placed on the sloping hearth of reverberatory furnace at a temperature just above the melting point of the metal. The pure metal flows down leaving behind the impurities. Sn, Pb, Bi are purified by this method.

Distillation Zn and Hg are purified by distillation under reduced pressure provided the impurities are non volatile.

Fractional Crystallisation (Zone Refining)



Impure metal rod is heated with the help of circular heater at one end. The metal melts and on cooling the pure metal gets solidified while impurities pass on into the molten zone. The process is repeated twice or thrice to get the pure metal.

Polling - The molten metal is stirred with green poles of wood, which liberates gas like methane. The latter reduces any oxide present in the metal eg CuO in the blister copper is reduced to copper.

Electrolytic Refining - The blocks of impure metal form the anode and pure metal form the cathode. Aqueous solution of appropriate salt is then electrolysed. On electrolysis at a suitable voltage the pure metal is deposited at cathode.

At anode : $M - ne^- \longrightarrow M^{n+}$

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

Cu, Sn, Ag, Pb, Cr, Ni are refined by this process.

Vapour Phase Refining- Metal is removed as volatile compound which is then decomposed by heating to get pure metal. e.g.

Mond's process

Ni is purified by this process.

$$Ni(s) + 4CO(g) \xrightarrow{300-350\ K} Ni(CO)_4(g)$$

$$Ni(CO)_4(g) \xrightarrow{450-470\ K} Ni(s) + 4CO(g)$$

Van Arkel process

Zr, Hf , Si, Ti and Be are refined by this process.

$$Zr(s) + 2I_2(g) \longrightarrow ZrI_4(g)$$

$$ZrI_4(g) \xrightarrow[\text{filament}]{\text{On hot}} Zr(s) + 2I_2(g)$$

Cupellation - This is the method of purifying silver containing lead as impurity. Impure silver is heated in a shallow (Cupel) which is made of bone ash under blast of air. Lead is easily oxidised and carried away by blast air. There are several chromatographic techniques such as gas chromatography, paper chromatography, etc.

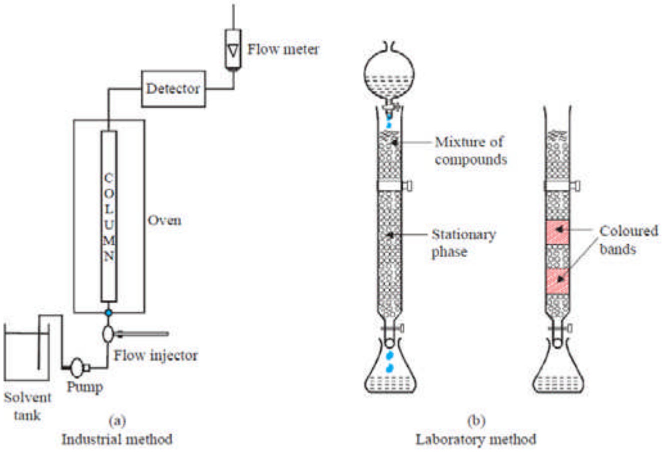
Desilverisation of Lead - Lead obtained from galena (PbS) contains impurities of silver, removal of which is called desilverisation .The processes employed are-

Parke's process -Lead containing silver is melted in iron pots and 1% Zn is added then cooled. Zn -Ag alloy solidifies and being light floats over molten lead and removed.

$$(Pb\ and\ Ag) + Zn \longrightarrow (Zn - Ag)\ alloy + Pb$$

Pattison's process - Lead containing less than 2.5% of Ag melts at lower temperature than lead. Thus, when an alloy of Pb-Ag containing more lead is melted then allowed to cool slowly, pure lead separates.

Chromatographic Methods - It is based on the preferential adsorption of different compounds on an adsorbent. The mixture is put in the liquid or gaseous medium which is moved through the adsorbent. The different compounds are adsorbed at different levels on adsorbent in column chromatography and recovered by using suitable solvent (eluent). The common adsorbent as Al_2O_3 or SiO_2 (silica). The least adsorbed component is recovered first. The method is very useful for purification of elements available in minute quantities.



Schematic diagrams showing column chromatography

SOME IMPORTANT TERMS USED IN METALLURGY

PYROMETALLURGY

In this process decomposition of the minerals and the extraction of the metal is brought about in dry state at high temperature by the action of heat. The steps employed are-

- Calcination
- Roasting
- Smelting
- Refining

Smelting is melting process that causes the materials to separate into two or more layers.

Two important kinds of layers are slag and molten metal. Iron is obtained by pyrometallurgy.

HYDROMETALLURGY

Extraction of metals from ores using aqueous solution. It includes-

- Leaching
- Reduction

Ag and Au are extracted by this process.

ELECTROMETALLURGY

Electrometallurgy is the process of obtaining metals through electrolysis. The electropositive metals are obtained by this method e.g. Na, Mg, etc.

Amalgamation

In this process the metal is extracted by using mercury. Most of the metals dissolve in Hg to form amalgams which when distilled in iron retorts leave behind free metal and Hg distills over

$$\text{Ore} + Hg \longrightarrow \text{amalgam} \xrightarrow{\text{distilled}} Hg + \text{metal}$$

Ag, Au, Pt form amalgam.

Thermit

It is mixture of Fe_2O_3 (3 parts) and Al powder (1part) when ignited with the help of barium peroxide, Fe_2O_3 is reduced to iron and an enormous amount of heat is produced due to exothermic nature of the reaction.

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe + 2500°C$$

The molten is utilised for welding and the process is known as thermit welding known as Goldschmidt Aluminothermic process.

Refractory Materials

The substance capable of withstanding at very high temperature without undergoing any deformation is called refractory material.

Acidic refractories - silica, quartz and sandstone

Basic refractories - lime ,dolomite and magnesite

Neutral refractories - chromite, bone ash and graphite.

Matte or Regulus

Artificially obtained sulphides are known as matte or regulus e.g. in extraction of copper.

Sulphating Roasting

It is partial oxidising roasting. Roasting of galena gives mixture of lead oxide and lead sulphate

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \longrightarrow 2PbSO_4$$

Chlorinating Roasting

Silver ores mixed with common salt when heated in presence of air, the chloride is obtained.

$$Ag_2S + 2NaCl \longrightarrow 2AgCl + Na_2S$$

Bessemerisation

The oxidation of impurities by passing the hot blast of air through molten metal in bessemer converter is called bessemerisation. Pig iron and copper are purified by this method.

Sintering

The conversion of small pieces of substances into larger one by partial fusion is known as sintering.

Pulverisation

The conversion of large pieces of a substance into small fine pieces or powder is known as pulverisation.

Anodizing

The process of forming an oxide coating on metal surface by making it an anode by electrolytic method in called anodizing.

Mode of Extraction of Some Metals

- Metals obtained by electrolytic reduction are - Li, Na, K, Mg, Ca , Al, Sr, Ba
- Metals obtained by reduction of oxides by carbon are - Zn from ZnO, Sn from SnO_2.
- Metals obtained by reduction of oxides by thermite process, (Alumino thermic process) are Cr from Cr_2O_3, Mn from Mn_3O_4.
- Metals obtained by air reduction method are - Hg from HgS, Pb from PbS.
- Metals obtained by precipitation method are - Ag, Au
- Metals obtained by reduction with Co, Fe
- Metals obtained by reduction with water gas are – Ni

Alloys

Alloys contain more than one element and have the characteristics of metals.

- Pure metals and alloys have different physical properties.
- Solution alloys are homogeneous mixtures and they are of two types
    - Substitutional alloys (Solute atoms take the positions of solvent atom)
    - Interstitial alloys (Solute atoms occupy interstitial sites)
- Heterogeneous alloys - Components are not dispersed uniformly e.g. pearlite steel

Relative Abundance

Abundance of elements in the earth's crust (by weight)

$$O > Si > Al > Fe \;\; Ca > Na > K > Mg > H > Ti > Cl > F$$

Abundance of elements in the earth's crust (in terms of number of atoms per 100 atoms)

$$O > Si > Al > H > Na > Ca > Fe > Mg > K >$$
$$Ti > C > Mn > S > F > Cl > Cr$$

Thermodynamic Principles of Metallurgy

Theory of metal lurgical transformations can be interpreted by Gibb‘s free energy change at any specified temp.

$$\Delta G = \Delta H - T\Delta S \text{ or } \Delta G^\circ = -RT\,\ell nK$$

where, ΔH = enthalpy change and

ΔS = entropy change

K = equilibrium constant at temp. T

The reducing agent is oxidised and metal oxide is reduced. The role of reducing agent is to provide ΔG° negative.

During reduction the metal oxide decomposes.

$$M_XO(s) \longrightarrow {}_XM \text{ (Solid or liquid)} + \frac{1}{2}O_2(g)$$

The reducing agent (C or CO) is oxidized

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

If net DG of two possible reactions (Reduction/Oxidation) is negative, the overall reaction will occur.

H.J.T. Ellingham diagram (plots of ΔG Vs T) provides a sound basis for considering the choic e of reducing agent in the reduction of oxides.

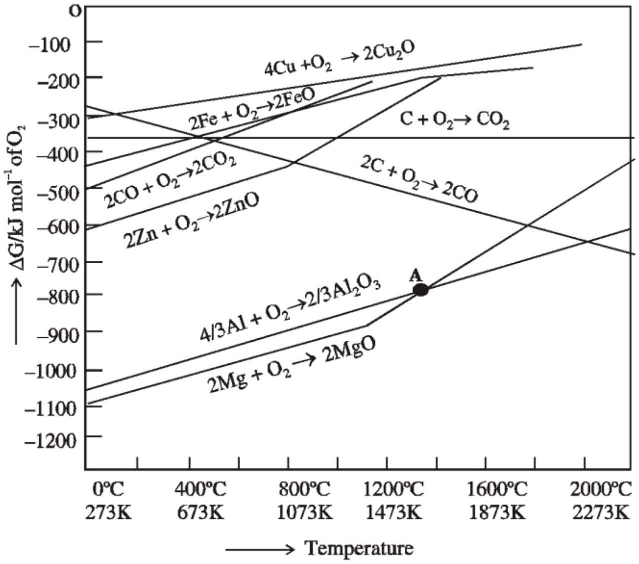


Fig. Gibbs energy (ΔG°) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

When alumina is reduced by magnesium, the two equations are

- $4Al + 3O_2 \longrightarrow 2Al_2O_3$
- $2Mg + O_2 \longrightarrow 2MgO$

DG becomes ZER O at the point of intersection of the Al_2O_3 and MgO curves (marked “A”). Above this point the magnesium can reduce alumina.

Note: Although thermodynamically feasible the magnesium metal, is not used for the reduction of aluminas. The temperature required would be so high and the process would be technologically difficult and uneconomic.

Limitations of Ellingham Diagram

It fails to predict the kinetics of reduction processes i.e. how fast it could be

- When the reactant/product are solid ΔG° cannot be interpreted by the equation

$$\Delta G^\circ = -RT \log K$$

Extraction of Iron From Its Oxides

The two simple reactions are-

- $FeO(s)\ Fe(s/\ell) + \frac{1}{2}O_2(g);\ \Delta G(FeO, Fe)$
- $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta G(C, CO)$

Adding the two reactions, we get

$$FeO(s) + C(s) \longrightarrow Fe(s/\ell) + CO(g)$$

$$\Delta G(FeO, Fe) + \Delta G(C, CO) = \Delta G$$

The resultant ΔG is –ve above 1073K (approx).

If the metal is obtained in liquid state the reduction becomes easier. (entropy increases and DG decreases).

Multiple Choice Questions

1. **A mineral is called ore if**

(a) The metal present in the mineral is costly

(b) A metal can be extracted from it

(c) A metal can be extracted profitably from it.

(d) A metal cannot be extracted from it.

2. **Which of the following is an ore of Fe?**

(a) Malachite	(b) Calamine
(c) Stellite	(d) Limonite

3. **Which of the following minerals is not an ore of Cu?**

(a) Cuprite	(b) Malachite
(c) Copper Pyrites	(d) Diaspore

4. The formula of copper pyrites is

(a) Cu_2O (b) $CuFeS_2$

(c) Cu_2S (d) $CuCO_3.Cu(OH)_2$

5. The electrolytic reduction technique is used in the extraction of

(a) Highly electronegative elements.

(b) Highly electropostive elements.

(c) Metalloids.

(d) Transition metals.

6. In the commercial electrochemical process for aluminium extraction, electrolyte used is

(a) $Al(OH)_3$ is NaOH solution.

(b) An aqueous solution of $Al_2 (SO_4)_3$.

(c) A molten mixture of Al_2O_3 and Na_3AlF_6.

(d) A molten mixture of Al_2O_3 and $Al(OH)_3$.

7. Which ore can be best concentrated by froth floatation process?

(a) Malachite (b) Cassiterite

(c) Galena (d) Magnetite

8. Electrolytic reduction of Al_2O_3 to Al by Hall- Herault process is carried out

(a) in presence of NaCl.

(b) in presence of fluorite.

(c) in presence of cryolite which forms a melt with lower melting point.

(d) in presence of cryolite which forms a melt with high melting point.

9. The chemical composition of 'slag' formed during the melting process in the extraction of copper is

(a) $Cu_2O + FeS$

(b) $FeSiO_3$

(c) $CuFeS_2$

(d) $Cu_2S + FeO$

10. Bessemer converter is used in the manufacture of

(a) Pig iron (b) Steel

(c) Wrought iron (d) Cast iron

11. The method of zone refining of metals is based on the principle of

(a) greater mobility of the pure metal than that of the impurity.

(b higher melting point of the impurity than that of the pure metal.

(c) greater noble character of the solid metal than that of impurity.

(d) greater solubility of the impurity in the molten state than in the solid.

12. In the leaching of Ag_2S with NaCN, a stream of air is also passed. It is because

(a) The reaction between Ag_2S and NaCN is reversible.

(b) to oxidise Na_2S formed in the reaction to Na_2SO_4.

(c) to oxidise Ag_2S to Ag_2O.

(d) Both (a) and (b).

13. Purest form of iron is

(a) Cast iron (b) Hard Steel

(c) Stainless steel (d) Wrought iron

14. Consider the following reaction at 1000° C

A. $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s)$ $\Delta G° = -360 \text{ kJ mol}^{-1}$

B. $C(gr) + \frac{1}{2}O_2(g)\ CO(g)$ $\Delta G° = -460 \text{ kJ mol}^{-1}$

Choose the correct statement at 1000°C

(a) Zinc can be oxidised by carbon monoxide.

(b) Zinc oxide can be reduced by graphite.

(c) Both statements (a) and (b) are correct.

(d) Both statements (a) and (b) are false.

ANSWERS and SOLUTIONS

1. (c) A metal can be extracted profitably from it.

2. (d) Limonite

3. (d) Diaspore

4. (b) $CuFeS_2$

5. (b) Highly electropostive elements.

6. (c) A molten mixture of Al_2O_3 and Na_3AlF_6.

7. (c) Galena

8. (c) in presence of cryolite which forms a melt with lower melting point.

9. (b) $FeSiO_3$

10. (b) Steel

11. (d) greater solubility of the impurity in the molten state than in the solid.

12. (d) Both (a) and (b).

13. (d) Wrought iron

14. (b) $C(gr) + \frac{1}{2}O_2(g)\ CO(g)$ $\Delta G° = -460 \text{ kJ mol}^{-1}$

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