

PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Minerals: These are naturally occurring chemical substances which are obtained from earth's crust by mining. In minerals metals are present in either native state or combined state.

Ores: The mineral from which metal can be economically and conveniently extracted is called ore.

Metallurgy: The entire scientific and technological process used for isolation of the metal from the ores is known as metallurgy. The major steps for extraction and isolation of metals are:--

- Concentration of the ore
- Isolation of metal from the concentrated ore
- Purification of metal

I) CONCENTRATION OF ORES

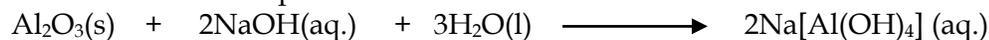
Removal of unwanted materials (ie; clay, sand etc.) from ores is known as concentration. These earthly or undesirable impurities are called GANGUE. Some important procedures are:-

- 1) Hydraulic washing: This is based on the difference in gravities of the ore and the gangue particles. In this an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and heavier ores are left behind.
- 2) Magnetic Separation: This is based on the differences in the magnetic properties of the ore components. One of the two, ore or gangue is capable of being attracted by magnetic field.
- 3) Froth Floatation process: This method is used to remove gangue from sulphide ores. A suspension of powdered ore is made with water. To it collectors (E.g- Pine oil) and Froth stabilizers (e.g., cresol, aniline) are added. Collectors enhance wettability of pine oil and froth stabilizers froth. Mineral particles wetted by oil are carried away with froth and gangue particles move into water.

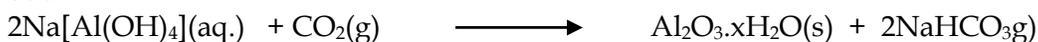
Two sulphide ores can be separated using depressants. For eg. NaCN is used to separate ZnS and PbS present in an ore.

4) Chemical Methods(Leaching):

a) Leaching of Alumina from Bauxite: Bauxite contains SiO_2 , iron oxides and titanium oxide as impurities. Powdered ore is treated with concentrated solution of NaOH at 478-523 K and 35-36 bar pressure.



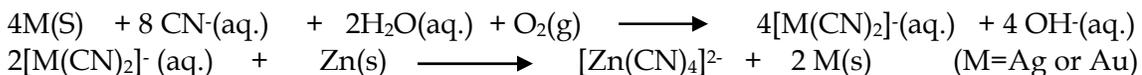
The aluminate solution is neutralized by passing CO_2 gas and hydrated Al_2O_3 separated out.



The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give pure Al_2O_3 .



b) Other example: In metallurgy of silver and gold, the respective metal is leached with dilute solution of NaCN or KCN in presence of air (Or O₂)



II) **CALCINATION/ROASTING**: The concentrated ore is then converted to its oxide form by heating .

If the concentrated ore is heated strongly in the absence of air to get rid of impurities, and the ore changes to oxide form, it is called calcination. It is generally observed for carbonate ore. $CaCO_3 \longrightarrow CaO + CO_2$

If the concentrated ore is heated in the presence of oxygen, ore gets converted to oxide form and small molecules like SO₂ are released. It generally takes place for sulphide ore. $ZnS + O_2 \longrightarrow ZnO + SO_2$

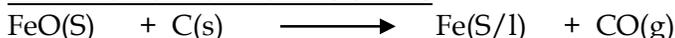
III) **REDUCTION**

Reduction of oxide to metal:

This involves heating of the oxide with a reducing agent like C or CO or even another metal based on reactivity of the metal to be extracted.



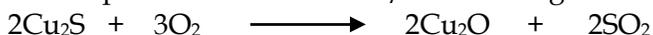
Extraction of iron from its oxides



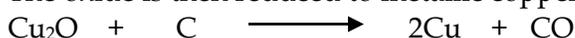
(Discussed later under extraction of Iron)

Extraction of copper from cuprous oxide:

The sulphide ores are roasted/smelted to give oxides (Most sulphide ores contain iron)



The oxide is then reduced to metallic copper using coke.



In actual process, the ore is heated in a reverberatory furnace after mixing with silica.

The iron oxide slags off as iron silicate and copper is produced in the form of copper matte. This contains Cu₂S and FeS.



Copper matte is then charged into silicalined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS₂, FeO and Cu₂S/Cu₂O to metallic copper. The reactions taking place are:



The solidified copper obtained has blistered appearance due to evolution of SO₂ & so is called blister copper.

Extraction of zinc from zinc oxide:

The reduction of zinc oxide is done using coke. For the purpose of heating, the oxide is made into brickettes with coke and clay.



The metal is distilled off and collected by rapid chilling.

Thermodynamic principles of metallurgy:

Gibb's energy is described by the equation $\Delta G = \Delta H - T\Delta S$.

For any reaction, this change can be described by $\Delta G = -RT \ln K$

Negative ΔG implies positive K and this can happen when reaction proceeds towards products.

- (i) If ΔS is positive, on increasing T the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and $\Delta H < T\Delta S$ and ΔG becomes negative.
- (ii) If reactants and products of two reactions are put together in a system and net ΔG is negative, overall reaction would occur. So the process involves coupling of two reactions and getting sum of their ΔG as negative.

For eg: In reduction of FeO



We couple the two so that net Gibb's energy change becomes



The resultant will have ΔG as negative.

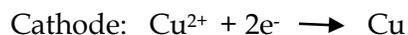
According to Ellingham diagram, the ΔG° Vs. T plot representing the reaction goes upward and that representing $\text{C} \rightarrow \text{CO}$ goes downward. At temp. above 1073 K the (C,CO) line come below the Fe, FeO line [$\Delta G_{(\text{C, CO})} < \Delta G_{(\text{Fe, FeO})}$]. So coke will be reducing FeO and is itself oxidized to CO.

IV) REFINING

A metal extracted by any method is usually contaminated with some impurity. Some methods are

- a) **Distillation:** The impure metal is evaporated to obtain pure metal as distillate. Used for low boiling metals like **Zn and mercury**.
- b) **Liquation:** The low melting metal, like **tin** is separated from high melting impurities by this method. The metal is made to flow on sloping surface.
- c) **Electrolytic refining:** In this method impure metal is made to act as anode. A strip of same metal in pure form is made cathode. The electrolyte used contains soluble salt of the same metal. The more basic metals remain in the solution and less basic form anode mud.

For e.g. **Copper** is refined by electrolytic method. Anode is impure copper and pure copper strips are taken as cathode and electrolyte is acidified solution of copper sulphate.

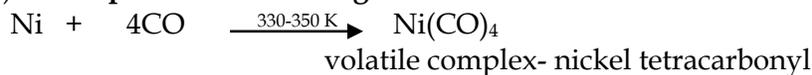


- d) **Zone refining:** It is based on the fact that melting point of a substance is lowered by the presence of impurities. Consequently when an impure metal in molten state is cooled, crystals of pure metal are solidified first and impurities remain behind in the

molten metal which crystallizes later. The semiconductors –silicon and germanium are purified by this method.

- e) **Vapour Phase refining:** This method is used for preparing ultrapure metals by forming vapours of the compound of metal and later decomposition to get pure metal.

Eg- 1) **Mond process for refining Ni**



At higher temperature,



- 2) **Van Arkel method for refining of Zr or Ti :** This method is useful for removing all oxygen and nitrogen present as impurity. Crude metal is heated in evacuated vessel with iodine.



Metal iodide is then heated on a tungsten filament to about 1800 K.



- f) **Chromatographic methods:** This method is based on the principle that different components are differently adsorbed on adsorbent. The mixture is put in a suitable solvent and applied on top of the column. The adsorbent is packed in a glass column. The adsorbed components are removed (eluted) out using suitable solvent (eluent). The weakly adsorbed component is eluted first followed by the more strongly adsorbed and so on. This is called column chromatography. This method is used for purification of elements available in minute quantities and impurities not very different in chemical properties.

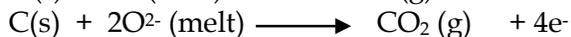
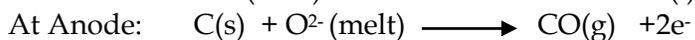
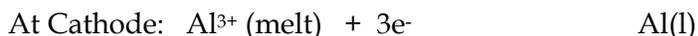
EXTRACTION OF ALUMINIUM:

Aluminium is extracted from bauxite ore, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. It involves two steps:

- Concentration (by Baeyer's Process) :** Purification of Bauxite ore is done by Baeyer's process. This Chemical method is called leaching.
(Explained under methods of concentration)
- Reduction { by Electrolysis of fused alumina (Hall-Heroult process)}:** The purified alumina is dissolved in molten cryolite and is electrolyse in an iron tank lined inside with carbon. The molten cryolite decreases the melting point to about 1173 K and also increases conductivity. The anode consists of a number of carbon rods which dip in fused electrolyte. The electrolyte is covered with a layer of powdered coke.



Reactions at electrodes are:



Therefore, aluminium is liberated at the cathode and gets collected at the bottom of the tank from where it is removed. The oxygen evolved combines with carbon of anode to form CO or

CO₂ and escapes out. Because of reaction at carbon anodes, these need to be replaced periodically.

3. Refining of Aluminium:

The aluminium metal obtained above is 99% pure, which is further purified by **Hoop's electrolytic method**. The process is carried out in an iron tank lined with carbon. It has 3 layers of molten liquid having different densities.

- (i) The top layer consists of pure Al having carbon electrodes dipping in it. The carbon electrodes act as cathode.
- (ii) The middle layer has fluorides of sodium, barium and Aluminium in molten state. This acts as an electrolyte.
- (iii) The bottom layer consists of impure Al along with the carbon lining acts as anode.

On passing electric current aluminium ions from the middle layer are discharged at cathode as pure Al. The pure Al is removed from the tapping hole. An equivalent amount of Al from bottom layer moves into the middle layer leaving behind impurities.

EXTRACTION OF IRON

Iron is the second most abundant element occurring in earth's crust. The common ores are:

Haemite Fe₂O₃

Magnetite Fe₃O₄

Limonite Fe₂O₃.3H₂O

Iron Pyrites FeS₂

Siderite FeCO₃

Cast Iron is usually extracted from its oxide ore (haematite). It involves the following steps---

- 1) **Concentration:** The ore is first crushed and crushed ore is concentrated by gravity separation; ie hydraulic washing
- 2) **Calcination:** The concentrated ore is calcined, ie, heated strongly in limited supply of air in a reverberatory furnace. The following changes take place:
 - i) Moisture is removed
 - ii) Impurities of S, P₄ and As are converted to their gaseous oxides; SO₂, As₂O₃ and P₄O₁₀ which are volatile and escape out.
- 3) **Reduction (by Smelting) :** The calcined ore is reduced with carbon, ie smelted in a blast furnace. It is a tall cylindrical furnace made of steel lined with fire bricks. It is narrow at the top and has cup and cone arrangement for the introduction of charge and outlet for waste gases. At the base of furnace, it is provided with ---
 - i) Tuyeres arrangement for introduction of hot air
 - ii) A tapping hole for withdrawing molten iron and
 - iii) An outlet through which slag is flown out.

The calcined ore (8 parts) is mixed with coke (4 parts) and limestone (1part) is introduced from top. At the same time a blast of hot air preheated at 1000 K is blown upwards with the help of tuyers arrangement. The added coke acts as a reducing agent and lime serves as flux. The burning of coke to carbon monoxide supplies most of the heat required for working temperature of furnace and give temp. upto 2200 K at the bottom of furnace. As the gases move up, they meet the descending charge and temp. falls. At the bottom reducing agent is carbon but at the top the reducing agent is CO.

The reactions occurring are:---

- 1) Combustion zone: At the base coke burns to produce CO₂ which starts rising upward. The reaction is exothermic and heat produced raises the temperature to about 2200 K.



- 2) Fusion zone: As CO₂ rises upward, it comes in contact with coke and gets reduced to CO.



The reaction is endothermic, the temperature is lowered to 1570 K. The iron produced in the upper region melts. Any Fe₂O₃ if present is reduced by hot coke to iron.



- 3) Slag formation zone; In the middle temperature is about 1270K. In this region limestone decomposes.

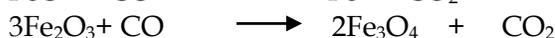


The lime acts as flux and combines with silica (present as an impurity) to produce slag.



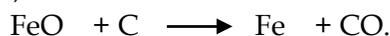
The molten slag forms a separate layer above molten iron.

- 4) Reduction Zone: The temperature near the top of furnace is 875 K. The oxide is reduced by carbon monoxide to iron.



The spongy iron produced moves down slowly and melts in fusion zone.

At lower hotter part, reaction is



It dissolves some carbon, silicon, phosphorus and manganese and forms a layer at the bottom. The iron obtained is called **Pig iron**.

Cast iron is different from Pig Iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly less carbon content (about 3%). It is extremely hard but brittle.

Wrought iron is purest form of iron and is prepared from cast iron by oxidizing impurities in reverberatory furnace lined with haematite. Haematite oxidizes carbon.



Limestone is added as flux and S, Si and P are oxidized and passed into slag. The metal is then removed.

EXTRACTION OF COPPER:

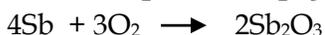
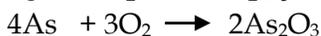
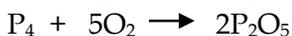
Copper is mainly extracted from copper pyrites (CuFeS₂). The various steps are:

- 1) **Crushing and concentration:** The ore is crushed in jaw crushers and is finally powdered. It is concentrated by froth floatation process.

- 2) **Roasting:** The concentrated ore is roasted, i.e., heated strongly in the presence of excess of air in a reverberatory furnace.

a) Moisture is removed from ore and it becomes dry.

b) The impurities of S, P, As and Sb are removed as their volatile oxides.

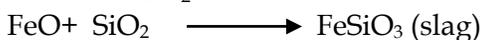
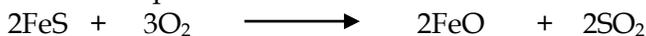


c) Copper pyrites is converted to ferrous sulphide (FeS) and cuprous sulphide (Cu₂S)



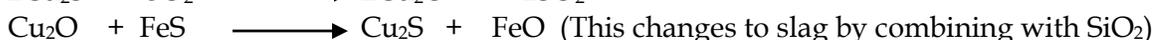
3) **Smelting:** The roasted ore is mixed with powdered coke and sand and is strongly heated in a blast furnace. The blast furnace is made of steel and is lined with fire bricks. A blast of hot air is introduced at the lower part of the furnace and changes occurring are:

a) Ferrous sulphide is oxidized to ferrous oxide which combines with silica to form slag.



The slag being lighter forms the upper layer and is removed from time to time.

b) During roasting if any oxide of copper is formed, it combines with FeS and is changed back into its sulphide



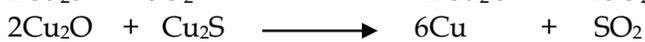
As a result two separate layers are formed at the bottom of furnace. Upper layer is slag which is removed as waste. The lower layer of molten mass contains mostly cuprous sulphide and some traces of ferrous sulphide. It is called matte and is taken out from tapping hole at bottom.

4) **Bessemerisation:** The molten matte from Blast-furnace is transferred to Bessemer converter. The vessel is made of steel lined inside with lime or MgO. A blast of hot air is mixed with sand is blown into molten matte. During this process

a) Traces of ferrous sulphide present in matte is oxidized to FeO which combines with silica to form slag.



b) Copper sulphide is oxidized to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.



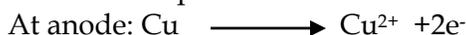
After the reaction has been completed, the converter is tilted and molten copper is put in moulds. The copper thus obtained is 99% pure and is known as blister copper. The name blister is given because as metal solidifies, the dissolved SO₂ escapes out producing blisters on metal surface.

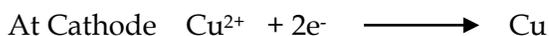
5) **Refining:** Blister copper is purified by:

a) **Poling:** Heating strongly in a reverberatory furnace in the presence of excess of air.

Impurities are either converted to oxides or converted to slag. Some copper also changes to cuprous oxide. This is reduced back to copper by stirring the molten metal with green poles of wood. This gives 99.5 % pure Cu, which is then purified by electrolytic refining.

b) **Electrolytic refining:** A thin sheet of metal is made cathode and block of crude metal is made as anode. Both the electrodes are placed in an acidified CuSO₄ solution when electric current is passed through the solution, impure Cu from anode goes into the solution and pure Cu from the solution gets deposited on the cathode.





The impurities of Zn, Ni, Fe etc. gets collected below as anode mud.

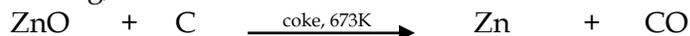
EXTRACTION OF ZINC

Principal ore of Zinc is Zinc Blende. Extraction is carried out in the following steps:-

- 1) **Concentration:** Ore is concentrated by froth floatation process.
- 2) **Roasting:** Concentrated ore is roasted in excess of air at about 1200 K and ZnS is converted to ZnO.



- 3) **Reduction:** ZnO is reduced by heating with crushed coke at 673 K. For the purpose of heating, the oxide is made into brickettes with coke and clay.



The metal is distilled off and collected by rapid chilling.

- 4) **Refining:** Impure metal is refined by electrolysis. In this process, impure zinc is made the anode and a plate of pure zinc is made the cathode. The electrolyte is zinc sulphate with little dil. H₂SO₄. On passing current zinc is deposited at cathode while equal amount of zinc from anode goes into electrolyte. Thus, pure zinc is obtained on cathode.

Some extractions based on oxidation:

1) EXTRACTION OF CHLORINE FROM BRINE

Chlorine is abundant in sea water and hence is obtained from electrolysis of brine solution.

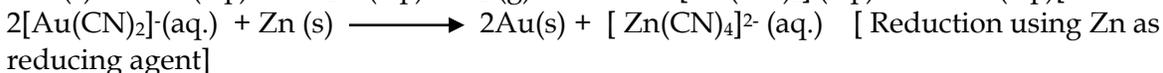
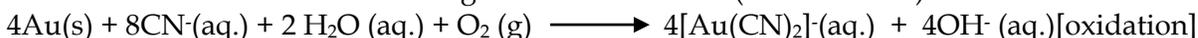


$$\Delta G^\circ = +422 \text{ KJ and using } \Delta G^\circ = -nFE^\circ_{\text{Cell}}, E^\circ = -2.2 \text{ V.}$$

So it requires emf greater than 2.2 V. But electrolysis requires an excess potential to overcome some hindering reaction. Thus, Cl₂ is obtained by electrolysis giving out H₂ and aqueous NaOH as by products.

2) EXTRACTION OF GOLD AND SILVER:

Extraction of Gold involves leaching the metal with CN⁻ (OXIDATION)



Similarly for Silver

