

REFINING OF METALS

Impurities generally present in extracted metals (except electrolytic reduction) are:

- Other metals
- Unreduced oxides of the metal
- Non-metals like carbon, silicon, phosphorus, sulphur etc.
- Flux or slag

Methods used in refining metals are:

- Liquation
- Poling
- Distillation
- Electrolytic refining

Liquation: Easily fusible metals like tin, lead etc. are refined by this process. In this method the impure metal is poured on the sloping hearth of a reverberatory furnace and heated slowly to a temperature little above the melting point of the metal. The pure metal drains out leaving behind infusible impurities.

Poling: Poling involves stirring the impure molten metal with green logs or bamboo. The hydrocarbons contained in the pole reduce any metal oxide present as impurity. Copper and tin are refined by this method.

Distillation: Volatile metals like zinc and mercury are purified by distillation. The pure metal distills over leaving behind non-volatile impurities.

Electrolytic Refining: Metals like copper, silver, zinc, tin etc. are refined by electrolysis.

Anode used- Block of impure metal

Cathode used- Thin sheet of pure metal

Electrolyte used- Suitable metal salt solution

On passing current pure metal deposits at the cathode sheet while more electropositive impurities are left in solution. Less electropositive (mainly precious noble metals) metals do not dissolve and fall away from the anode to settle down below as anode mud.

Copper Refining:

Anode: Impure copper

Cathode: Thin piece of pure copper

Electrolyte: acidified solution of CuSO_4

Aluminium Refining (Hoope's Electrolytic process):

This process uses an electrolytic cell which contains three layers of molten substances of different specific gravity.

Bottom layer- Molten impure aluminium. It contains carbon lining and serves as the anode.

Middle layer- Mixture of fluorides of sodium, barium and aluminium.

Top layer- Pure molten aluminium with carbon electrodes which serves cathode.

On passing current aluminium from the middle layer passes to the top layer and an equivalent amount of it shifts from the lower to the middle one. Pure aluminium is tapped from the top.

HYDROMETALLURGY

Hydrometallurgy is a method for obtaining metals from their ores. It is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates and recycled or residual materials. It is typically divided into three general areas.

- Leaching
- Solution Concentration and purification
- Metal or metal compound recovery

Leaching: This method involves the use of aqueous solution (lixiviant solution) to extract the metal from metal bearing materials. The lixiviant solution generally contains chelating agents like amines or Schiff bases. The conditions of this solution are optimized with respect to their pH, redox potential, nature of chelating agent and temperature. Five basic leaching reactors are:

- In-situ leaching
- Tank leaching
- Heap leaching
- Autoclave leaching
- Vat leaching

Solution Concentration and Purification:

After leaching, the leached liquor most normally undergoes concentration of metal ions that are to be recovered. Additionally undesirable metal ions sometimes require removal.

Methods:

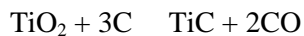
- Precipitation: It is selective removal of a compound of the targeted metal or removal of a major impurity by precipitation of one of its compounds. {Copper is precipitated as its sulphide as a means to purify nickel leachates. }
- Concentration: Conversion of the metal ion to the metal by a redox reaction. {Addition of scrap iron to a solution of copper ions leads to the dissolution of iron and copper is deposited. }
- Solvent Extraction: A mixture of an extractant and a diluent (generally some type of oil) is used to extract a metal from one phase to another. This mixture is referred to as organic.
- Ion exchange: In this method chelating agents, natural zeolites, activated carbon, resins and liquid organics impregnated with chelating agents are all used to exchange cations or anions with the solution.
- Gas reduction: Treating a solution of nickel and ammonia with hydrogen affords nickel metal as its powder.
- Electrowinning: Expensive electrolytic process is applied for isolation of precious metals.

Metal recovery:

It is the final step of hydrometallurgical process. Metals suitable for sale as raw materials are often directly produced in this step. The methods used are electrolysis, gaseous reduction and precipitation.

KROLL PROCESS:

Though from Ellingham diagram we can conclude that TiO_2 can be reduced by carbon-reduction process but practically it is not possible because TiO_2 on carbon reduction in air forms titanium carbide and nitride. (Metallic Ti is highly reactive and forms carbides and nitrides readily)



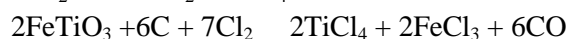
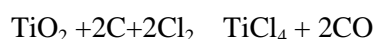
Moreover metallic Ti reacts with every refractory material.

Extraction of titanium:

Ores used: Ilmenite (FeTiO_3) and Rutile(TiO_2)

Steps involved:

1. Conversion of the ores to TiCl_4 :



2. Separation of TiCl_4 from FeCl_3 in case of ilmenite:

TiCl_4 (b.p- 137°C) and FeCl_3 (sublimes at 285°C) mixture is fractionally distilled when TiCl_4 is separated out.

3. Reduction of TiCl_4 (Kroll Process):

TiCl_4 is treated with molten Mg in argon atmosphere at about $1000\text{-}1150^\circ\text{C}$ when spongy mass of Ti is produced along with MgCl_2 . MgCl_2 and excess Mg are removed by washing with water and dilute HCl. They can also be separated by distillation. In original Kroll process reduction was done by calcium. At present sodium is also used instead of Mg where NaCl is obtained which is removed by washing with water.

4. Purification of spongy Titanium:

Spongy Ti is melted under argon or high vacuum in an electric arc furnace to get solid Ti which is casted into ingots.

van Arkel-de Boer Process (example of vapour- phase refining process):

This process, also known as Crystal Bar process or iodide process was developed by Anton Edward van Arkel and Jan Hendrik de Boer in 1925. This process was the first industrial process for the commercial production of pure ductile metallic zirconium. It is used in the production of small quantities of ultrapure titanium and zirconium. It primarily involves the formation of metal iodides and their subsequent decomposition to yield pure metal. The apparatus used is an evacuated quartz glass vessel with molybdenum electrodes and a tungsten filament.

Impure Ti/Zr is heated in the vessel with I_2 at $50^\circ\text{C}\text{-}250^\circ\text{C}$ to produce $\text{TiI}_4/\text{ZrI}_4$. The b.p of the iodides are lowered in reduced pressure. The iodides are heated up to 1400°C by white hot tungsten filament when the gaseous iodides decompose to give the ultrapure metal which deposits on the tungsten filament. The impurities are left behind in the vessel.

MOND'S PROCESS

Mond's process or the carbonyl process was developed by Ludwig Mond in 1890. It is an example of vapour phase refining process. This process is used to prepare highly pure nickel metal.

Nickel used in this process is obtained as sulphide in a matte along with copper sulphide after roasting and smelting of a sulphide ore containing ~3% Ni, 1.5% Cu, chalcopyrites, other iron sulphides and some precious metals.

At first Ni-Cu sulphide is roasted to give Ni-Cu oxides which are then leached with dilute H_2SO_4 . CuO is mostly removed as CuSO_4 . The residual NiO with a little amount of CuO is treated with water gas at $300\text{-}350^\circ\text{C}$ where both the metal oxides are converted to the respective metals by H_2 . The impure Ni now reacts with CO of the water gas at 20atm pressure and 150°C temperature to give gaseous $\text{Ni}(\text{CO})_4$ (nickel tetracarbonyl). The

impurities are left behind as solids. The mixture of $\text{Ni}(\text{CO})_4$ and water gas is heated to 230°C where $\text{Ni}(\text{CO})_4$ decomposes resulting in deposition of 99.95% pure nickel. The CO is recycled.

PARTING PROCESS:

Parting in metallurgy is the separation of gold and silver by chemical or electrochemical means. Gold and silver are often found together in the slimes left over from copper refining or as a metallic by-product of lead or zinc smelting. The solid mixture of the two is known as bullion.

Chemical Parting:

The bullion is boiled in nitric acid where silver is removed as silver nitrate and gold is left as residue. The filtrate is treated with ferrous sulphate when silver is precipitated out.

Electrochemical parting:

The bullions are cast into anodes and placed in an electrolytic cell. On passing electric current more noble metals and a little amount of silver is left as anode mud. The silver metal dissolves in electrolyte and then deposits in the cathode. The anode mud is boiled in sulphuric acid and KNO_3 is added to dissolve silver. Gold is thus left behind.

Therefore parting may be defined as a corrosion process in which the more active metal is selectively removed from the alloy leaving behind a porous weak deposit of the more precious metal. This process of selective removal is most efficiently used in the alloys which contain metals which are quite apart in electrochemical series, e.g. zinc and copper in brass. When parting is used for leaching of zinc in brass the process is called dezincification.

ZONE-REFINING:

The zone-refining process is based on the principle that the impurities in a metallic block are more soluble in the melt state (i.e. the molten state) than compared to the corresponding solid state.

In the zone refining process a circular mobile heater is fixed at one end of the metal rod which is fixed at one end of the metal rod which is made up of the impure metal. The metallic impurities melt at the temporary position of the heater (i.e. at one end). As the heater moves forward the melt containing the impurities (as the impurities are more soluble in the melt) also moves forward. The heater slowly moves along the entire rod. The pure metal is left to solidify behind as the heater moves along. The concentration of the impurities in the melt increases as the heater moves forward. Finally the impurities are accumulated at the other end of the rod. The process is repeated multiple times in the same direction. Lastly the end of the rod where impurities have accumulated is cut off. The process is used for manufacture of ultrapure silicon, germanium and gallium.

