General Principles and Processes of Isolation of Elements - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Appreciate the Need for Refining of Metals
- Enlist Different Methods of Refining of Crude Metals
- Select Specific Methods for Refining according to the Properties of Metal

Contents Outline

- General Introduction
- Distillation
- Liquation
- Electrolytic Refining of Metals
- Vapour Phase Refining
- Zone Refining
- Chromatographic Methods
- Uses of Aluminium, Copper, Zinc and Iron
- Summary

Introduction

A metal extracted by any method from its concentrated ore is usually contaminated with some impurity. Impurities present reduce electrical and thermal conductivity and are not suitable for use in the industry as such. The impure or crude metal obtained after reduction of the ore may contain:

i. Some residual unchanged ore.
ii. Some other metals present in smaller amount in the ore.
iii. Residual slag, flux etc. left after smelting.
iv. Non metals like carbon, silicon, phosphorus, sulphur etc.

For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

(a)	Distillation	**(b)**	Liquation

(c)	Electrolysis	**(d)**	Zone refining
(e)	Vapour phase refining	**(f)**	Chromatographic methods

These are described in detail here.

Distillation

This method is very useful for metals with low boiling point, i.e. metals like zinc, cadmium and mercury which are easily volatile. The impure metal is heated in absence of air in a retort and the vapours are condensed and collected in a receiver. The non volatile impurities are left behind in the retort. The impure metal is evaporated to obtain the pure metal as distillate.

Process

- The metal to be refined is heated above its boiling point
- Impurities do not vaporise
- Pure metal vaporises and is condensed
- Impurities are left behind

Liquation

This method is used to purify metals having a low melting point; like Bismuth, Tin, lead, mercury etc. The impure metal is made to flow on the sloping hearth of a furnace and gently heated in an inert atmosphere (absence of oxygen). The impurities which are less fusible than the metal are left behind on the top of the hearth whereas the fusible metal flows down. In this way metal is separated from higher melting impurities (Figure 1).

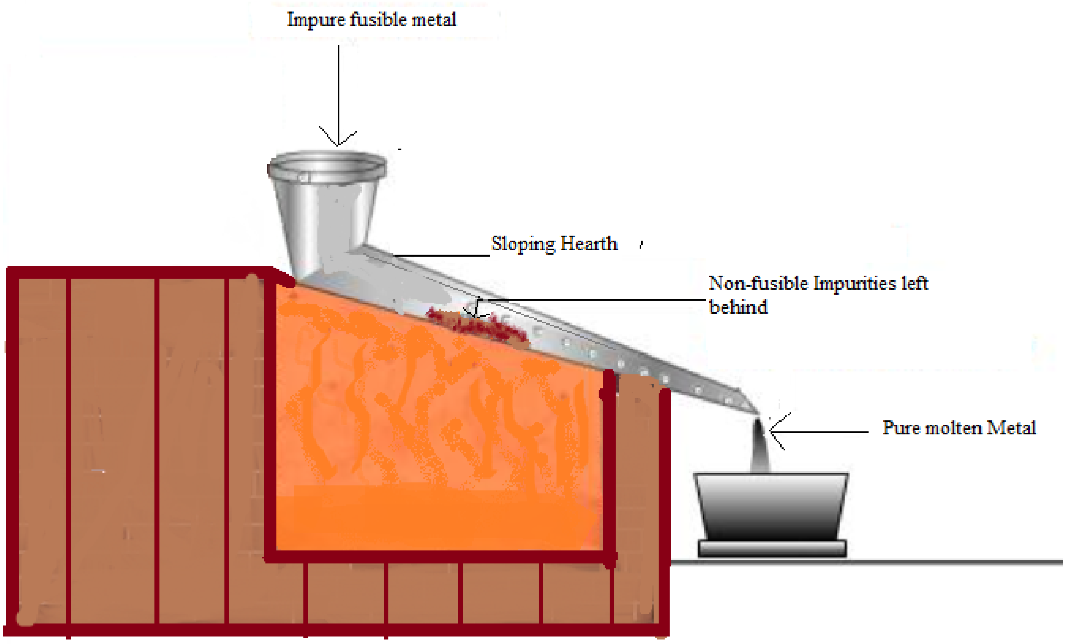


Figure 1: Liquation Method

Process

- The metal to be refined is placed over the sloping hearth of a furnace
- The temperature of the furnace is maintained slightly above the melting point of the metal
- Pure metal melt and flow down
- Impurities, having higher melting point, are left behind

Electrolytic Refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as a cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy which you have studied previously. The reactions are

Anode: $M \rightarrow M^{n+} + ne^{-}$

Cathode: $M^{n+} + ne^{-} \rightarrow M$ (1)

Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

Anode: Impure blister copper

Cathode: Thin sheets of copper

Electrolyte: An aqueous solution of copper sulphate containing H_2SO_4

Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (2)

On passing electric current, pure copper metal from the electrolyte solution deposits on the cathode. At the same time an equal amount of impure copper dissolves from anode into the electrolyte solution. The metallic impurities present in the blister copper drop down and deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining (Figure 2).

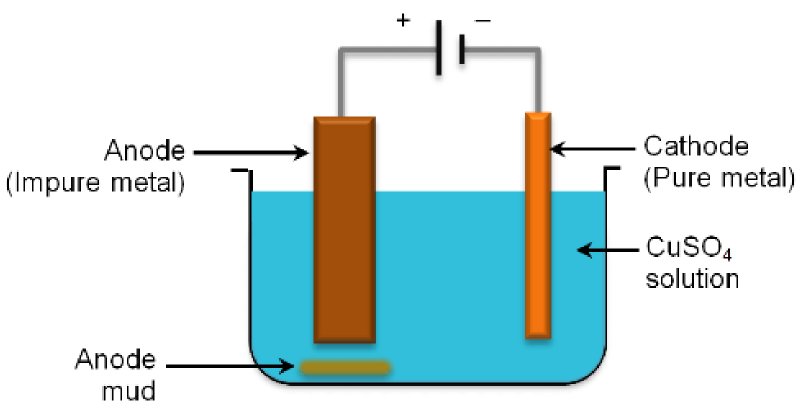


Figure 2: Electrolytic refining

Zinc, silver, aluminium and lead may also be refined this way. The metals obtained are of very high purity of the order of 99.9% pure.

Zone refining

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal (Figure 3).

The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction.

At one end, impurities get concentrated. This end is cut off.

This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

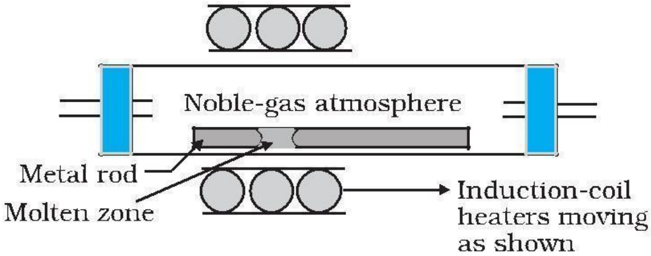


Fig. 3: Zone refining process

Vapour Phase Refining

In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are:

- The metal should form a volatile compound with an available reagent,
- The volatile compound should be easily decomposable, so that the recovery is easy.

Following examples will illustrate this technique.

Mond Process for Refining Nickel

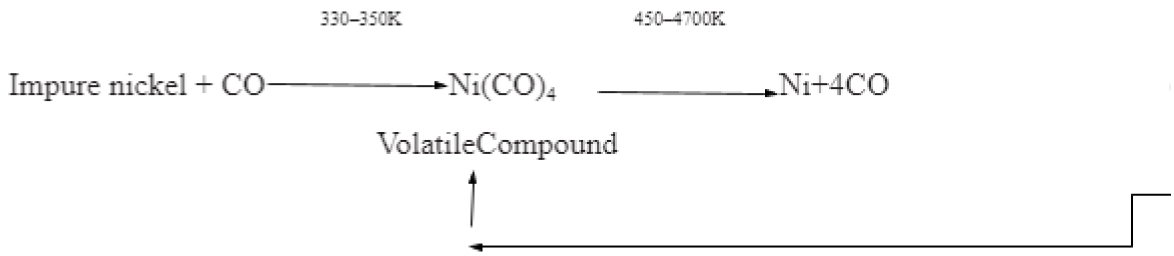
In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:

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

The carbon monoxide is recycled in the process as shown above. (5)



Van Arkel Method: This method is used for obtaining ultra pure metals **for Refining Zirconium or Titanium**: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4 \quad (6)$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2 \quad (7)$$

Applications of Ultra Pure Zr and Ti

Zirconium is used in alloys such as zircaloy, which is used in nuclear applications since it does not readily absorb neutrons. It is also used in catalytic converters, percussion caps and furnace bricks. The major end uses of zircon ($ZrSiO_4$) are refractories, ceramic opacification and foundry sands. Zircon is also marketed as a natural gemstone used in jewellery. The metal also has many other uses, among them in photographic flashbulbs and surgical instruments, to make the glass for television, in the removal of residual gases from electronic vacuum tubes, and as a hardening agent in alloys, especially steel. The paper and packaging industries are finding that zirconium compounds make good surface coatings because they have excellent water resistance and strength.

Read more: http://www.lenntech.com/periodic/elements/zr.htm#ixzz4WTnS9I00

Titanium can be alloyed with other elements, to produce strong, lightweight alloys for jet engines, missiles and spacecraft, industrial process orthopedic implants, dental and endodontic instruments and files, sporting goods and jewellery.

The main physical property of both Titanium and Zirconium which belong to the same group is that they are resistant to corrosion and have a high strength-to-density ratio.

Read more: http://nanocon2013.tanger.cz/files/proceedings/nanocon_10/lists/papers/641.pdf

Chromatographic Methods

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. The selective distribution of the various components of a mixture between stationary and mobile phase is the principle behind this technique. The stationary phase may be a solid or a tightly bound liquid on a solid support. The liquid phase may be a gas or a liquid. The most common chromatographic methods are:

(i) Paper chromatography
(ii) Thin layer chromatography
(iii) Gas chromatography
(iv) Column chromatography

Column Chromatography

It is one of the simplest chromatographic methods.

Principle: Difference in the extent of adsorption of various constituents present in a mixture on the stationary phase (adsorbent).

Common adsorbents: alumina, silica gel, magnesium oxide, cellulose powder, active animal charcoal etc.

Process: The steps are as follows:

a. Preparation of adsorbent column
b. Adsorption
c. Elution of components and recovery.

a. **Preparation of adsorbent column:** Cotton wool or glass wool plug is placed near the bottom of a burette. On the top of it the adsorbent material is packed. This forms the stationary phase.

b. **Adsorption**: A concentrated solution of the mixture to be separated is placed on the top layer of the adsorbent column and pure solvent is poured slowly over it. As the solvent passes through the top layer it dissolves the mixture and takes it down as it flows through the adsorbent. Consequently the components separate into a number of individual layers called bands depending upon the extent of adsorption of the components. Each band is called a **chromatogram**.

c. **Elution of components and recovery**: The adsorbed components are removed (**eluted**) by using suitable solvents (**eluant**). The process of collecting the components separately after opening the stop cock of the burette is known as elution.

In a nutshell, in this process, different components are adsorbed at different levels on the column. Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method* is given the name. In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

Procedures followed in column chromatography have been depicted in Fig. 3.

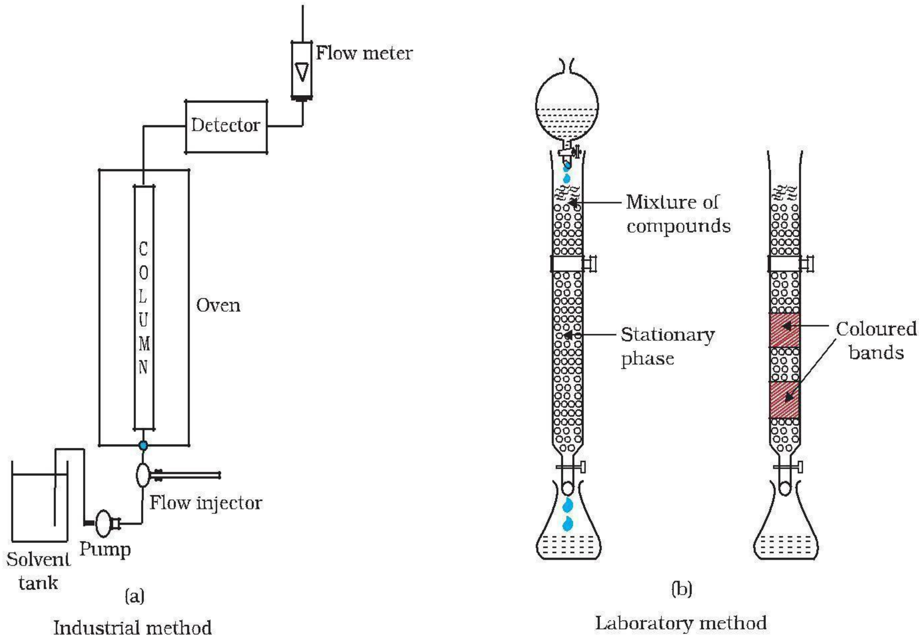


Fig. 4: Schematic diagrams showing column chromatography

Taking it the other way, chromatography in general, involves a mobile phase and a stationary phase. The sample or sample extract is dissolved in a mobile phase. The mobile phase may be a gas, a liquid or a

Looking it the other way, chromatography in general, involves a mobile phase and a stationary phase. The sample or sample extract is dissolved in a mobile phase. The mobile phase may be a gas, a liquid or a supercritical fluid. The stationary phase is immobile and immiscible (like the Al_2O_3 column in the example of column chromatography above). The mobile phase is then forced through the stationary phase. The mobile phase and the stationary phase are chosen such that components of the sample have different solubilities in the two phases. A component which is quite soluble in the stationary phase takes longer time to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase. Thus sample components are separated from each other as they travel through the stationary phase. Depending upon the two phases and the way sample is inserted/injected, the chromatographic technique is named.

Uses of Aluminium, Copper, Zinc and Iron

Aluminium: Aluminium foils are used as wrappers for chocolates. The fine dust of the metal is used in paints and lacquers. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminium are used as electricity conductors. Alloys containing aluminium, being light, are very useful.

Copper: Copper is used for making wires used in the electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Zinc: Zinc is used for galvanising iron. It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and German silver (Cu 25-30%, Zn 25-30%, Ni 40–50%). Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Iron: Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes , toys, etc. It is used in the manufacture of wrought iron and steel. Wrought iron is used in making anchors, wires, bolts, chains and agricultural implements. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

Summary

For getting pure metals we require refining. Refining process depends upon the differences in properties of the metal and the impurities. Several methods are employed in refining the metal.

For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with NaOH. Sodium aluminate thus formed is separated and then neutralised to give back the hydrated oxide, which is then electrolysed using cryolite as a flux. Extraction of iron is done by reduction of its oxide ore in blast furnace. Copper is extracted by smelting and heating in a reverberatory furnace. Extraction of zinc oxides is done using coke. Several methods are employed in refining the metal. Some of them are listed below.

(a) Distillation (b) Liquation

(c) Electrolysis (d) Zone refining

(e) Vapour phase refining (f) Chromatographic methods

Metals, in general, are very widely used and have contributed significantly in the development of a variety of industries.