# GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS REFINING OF METAL

# PURIFICATION OR REFINING OF METALS

Metals obtained by reduction processes still contain some objectionable impurities and have to be refined. Numerous techniques are available, including the following:

## PHYSICAL METHODS

These methods include the following processes:

**(I) Liquation Process:** This process is used for the purification of the metal, which itself is readily fusible, but the impurities are infusible.

**Examples:** (a) Purification of impure tin metal

(b) Purification of crude zinc

- (II) Fractional Distillation Process: This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.
- (III) Zone Refining Method (Fractional Crystallization Method): This process is used when metals are required in very high purity. For example, pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.
- **(IV) 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.

#### **CHEMICAL METHODS**

These methods include the following methods:

# (I) OXIDATIVE REFINING:

The method is used when the impurities present in the metal have a greater affinity for oxygen and are more readily oxidized than the metal.

#### (i) Bessemerization (Purification of iron) :

The iron obtained from a blast furnace is a brittle material called cast iron or pig iron. Molten iron from blast furnace is exposed to a jet of pure  $O_2$  gas for about 20 minutes in a furnace that is lined with basic oxide such as CaO. The impurities in the iron are oxidized and the acidic oxides that form react with basic CaO to yield a molten slag that can be poured off. Phosphorous, for example, is oxidized to  $P_4O_{10}$ , which then reacts with CaO to give molten Ca<sub>3</sub> (PO<sub>4</sub>)<sub>2</sub>.

> $P_4(l) + 5 O_2(g) \rightarrow P_4O_{10}(l)$ 6 CaO (g) + P\_4O\_{10}(l) → 2 Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(l) Basic oxide acidic oxide slag

(ii) Cupellation (Removal of Lead) :

In this process the molten impure metal is heated in a cupel, which is boat-shaped dish made of bone ash or cement, and a blast of air is passed over the molten metal. The impurities are oxidized and the volatile oxides thus produced escape with the blast of air. The pure metal remains behind in the cupel. Pb present in silver is removed by cupellation process.

 $2 \operatorname{Pb}(g) + O_2 \longrightarrow 2 \operatorname{PbO}(g)$ 

#### (II) PARTING PROCESS:

Crude gold obtained by MacArthur-Forrest cyanide and chlorination process contains Ag, Cu, Zn, and sometimes Pb as impurity. Zn and Pb are removed by cupellation process. Cu and Ag are removed by parting process.

(i) Parting with sulfuric acid or nitric acid: Gold is not attacked by these acids while Cu and Ag dissolve. If, however, the Au content in an impure sample is more than 30%, the Cu and Ag are also not attacked by the acid of any strength. Hence, before the acid treatment, the impure sample is melted with necessary amount of Ag to reduce its gold content to about 25% (quartation). The resulting alloy, after being granulated in water, is boiled with H<sub>2</sub>SO<sub>4</sub> or nitric acid when Cu and Ag pass into solution, leaving Au undissolved. Au is separated and fused again with borax and nitre when 100% Au is obtained. (ii) Parting with CI<sub>2</sub>: Sometimes chlorine is used for the purification of Au. The impure sample of Au is fused with borax and CI<sub>2</sub> gas is forced through it. The base metals are converted into chlorides that pass out as fumes at this high temperature, and AgCI forms a separate layer between the fused layer of Au and borax, which is skimmed off and the Au left behind cast into ingots.

## (III) POLING PROCESS:

This process is used for the purification of copper and tin.

(i) Purification of Impure Copper : Impure copper is remelted in a reverberatory furnace lined with SiO<sub>2</sub> and a blast of O<sub>2</sub> is blows into the furnace. O<sub>2</sub> oxidises S, Sb and As to their respective oxides which, being, volatile, get volatilised and are thus removed. Fe is oxidised to FeO which forms a slag of FeSiO<sub>3</sub> with SiO<sub>2</sub> lining of the furnace. Molten copper left behind contains CuO as impurity. This molten copper is treated with powdered anthracite and then stirred with a pole of green wood. Green wood, at high temperature, liberates hydrocarbon gases, which are converted into methane (CH<sub>4</sub>). Methane thus obtained reduces CuO to free Cumetal, which is about 99.5% pure and is called tough pitch copper.

Green wood  $\rightarrow$  Hydrocarbons  $\rightarrow$  CH<sub>4</sub>

 $4CuO + CH_4 \rightarrow 4Cu$  (pure metal) +  $CO_2 + 2H_2O$ 

(ii) Purification of Impure Tin: Impure tin metal contains the impurities of Cu, Fe, W and SnO<sub>2</sub>. The impurity of SnO<sub>2</sub> is due to the incomplete reduction of tin stone ore (SnO<sub>2</sub>) during smelting. In order to remove these impurities, the impure molten tin metal is taken in a big pot and stirred with a pole of green wood. Green wood, at high temperature liberates hydrocarbon gases, which are converted into methane CH<sub>4</sub>. Methane thus obtained reduces SnO<sub>2</sub> to pure metal while the impurities of Cu, Fe, W etc. come up to the surface, where they come in contact with air and are oxidised to their respective oxides. The oxides form a scum on the surface of pure tin metal. This scum is removed from the surface. Tin metal obtained by this method is 99% pure.

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Green wood  $\rightarrow$  Hydrocarbon  $\rightarrow$  CH<sub>4</sub> 2SnO<sub>2</sub> + CH<sub>4</sub> $\rightarrow$  2Sn + CO<sub>2</sub> + 2H<sub>2</sub>O

## (IV) ELECTROLYTIC REFINING:

Some metals such as Cu, Ni, and Al are refined electrolytically. The Hooper process is a process for the electrolytic refining of aluminum. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing aluminum fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminum ion  $(Al^{3+})$ , and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminum is drawn off the top.

At anode : Al 
$$\longrightarrow$$
 Al<sup>3+</sup> + 3e<sup>-</sup>  
At cathode: Al<sup>3+</sup> + 3e<sup>-</sup> Al

Copper obtained from the reduction of ores must be purified for use in making electrical wiring because impurities increase its electrical resistance. The method used is electro-refining.

Impure Cu obtained from ores is converted to pure Cu in an electrolyte cell that the impure copper as the anode and pure copper as the cathode. The electrolyte is an aqueous solution of CuSO<sub>4</sub>. At the impure Cu anode, Cu is oxidized along with the more easily oxidized metallic impurities such as Zn and Fe. The less easily oxidized impurities such as Ag, Au, and Pt fall to the bottom of the cell as anode mud, which is reprocessed to recover the precious metals. At the pure Cu cathode,  $Cu^{2+}$  ions get reduced to pure copper metal, but the less easily reduced metal ions ( $Zn^{2+}$ ,  $Fe^{2+}$  etc.) remain in the solution.

Anode (oxidation):  $M(s) \rightarrow M^{2+}(aq) + 2e^{-}(M = Cu, Zn, Fe)$ 

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

Thus, the net cell reaction simply involves transfer of Cu metal from the impure anode to the pure cathode, Cu obtained by this process is 99.95% pure.

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## (V) KROLL'S PROCESS:

$$\text{TiCl}_4 + 2 \text{ Mg} \xrightarrow{1000 - 1500^{\circ}C} \text{Ti} + 2 \text{ MgCl}_2 \text{ (Kroll's process)}$$

 $TiCl_4 + 4 \text{ Na} \xrightarrow[under atmo sphere of Argon]} Ti + 4 NaCl (Imperial metal industries)$ 

(IMI) process)

NaCl is leached with H<sub>2</sub>O. Ti is in the form of small granules. Zr is also produced by Kroll's process.

# (VI) VAPOUR PHASE REFINING:

(i) Extraction of Nickel (Mond's process) :

Ni(s) + 4 CO(s)  $\xrightarrow{50^{\circ}C}$  [Ni(CO<sub>4</sub>)] (g) [Ni (CO)<sub>4</sub>](g)  $\xrightarrow{200^{\circ}C}$  Ni + 4CO(g)

# (ii) Van Arkell-De Boer Process:

Small amounts of very pure metals (Ti, Zr, or Bi) can be produced by this method.

Impure Ti +  $2I_2 \xrightarrow{50-250^{\circ}C}$  TiI<sub>4</sub>  $\xrightarrow{1400^{\circ}C}$  Ti +  $2I_2$ 

## (VII) PARKES PROCESS:

The removal of the impurities of Ag from the commercial lead is called desulfurization of lead and is done by Parkes Process. Thus, Parkes process is the desulfurization of lead.

In Parkes process, the commercial lead, which contains Ag as impurities, is melted in iron pots and 1% of Zn is added to it. The molten mass is thoroughly agitated. Since Ag is about 300 times more soluble in Zn than in Pb, most of the Ag present in the commercial lead as impurity mixes with Zn, to form Zn–Ag alloy. When the whole is cooled, two layers are obtained. The upper layer contains Zn–Ag alloy in the solid state, while the lower layer has lead in the molten state. This lead contains only 0.0004% of Ag and hence is almost pure. Lead obtained after removing most of Ag from it (desulfurization of lead) by Parkes process, is called desilverised lead. This lead contains the impurities of metals like Zn, Au, Sb etc. These metal impurities are removed from deliveries lead by Bett's Electrolytic Process.

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Zn–Ag alloy, formed in the upper layer, is skimmed off from the surface of the molten lead by perforate ladles. This alloy contains lead as impurity. This impurity of Pb is removed from the alloy by liquation process, in which Zn–Ag alloy is heated in a slopping furnace, when the impurity of Pb melts and hence drains away from the solid alloy. Thus purified Zn–Ag is obtained. Now Ag can be obtained from this purified Zn– Ag alloy by distillation process, in which the alloy is heated strongly in presence of little carbon in a fire–clay retort. Zn, being more volatile, distills off while Ag remains in the retort, carbon used in the process reuses the oxide of Zn, if formed. Ag obtained from Zn–Ag alloy is contaminated with a little of Pb as impurity. This impurity of Pb placed in a cupel (cupel is a boat–shaped) dish made of bone ash which is porous in nature) in a reverberatory furnace and heated in the presence of air. By doing so, lead (impurity) is oxidised to PbO (litharge) which volatilizes and pure Ag is left behind in the cupel. Last traces of PbO are absorbed by the porous mass of the cupel.

#### (VIII) PUDDING PROCESS:

This process is used for the manufacture of wrought iron from cast iron. We know that cast iron contains the impurities of C, S, Si, Mn and P. When these impurities are removed from cast iron, we get wrought iron. In this process the impurities are oxidised to their oxides not by blast of air but by the hematite (Fe<sub>2</sub>O<sub>3</sub>) lining of the furnace.