Electrolytic refining Method

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as 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. The reactions are :

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

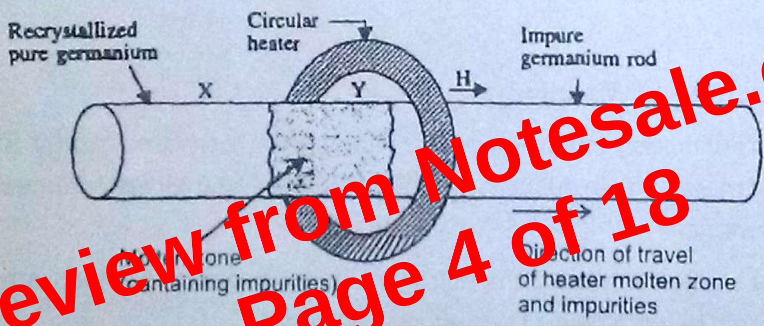
Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolysis is the transfer of copper in pure form from the anode to the cathode :

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

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; Zinc, silver and Lead may also be refined by this methode.

Zone refining Method

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. 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.



Zone refining of germanium metal

Van-Arkel Method (Vapour phase refining)

In this method, the metal is converted into its volatile compound and collected in some vessel. It is then decomposed to give pure metal. The two requirements for this are :

(i) the metal should form a volatile compound with an available reagent,

(ii) the volatile compound should be easily decomposable, so that the recovery is easy.

Mond process for refining nickel; In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl;

$$Ni + 4CO \xrightarrow{50°C} Ni(CO)_4$$

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

$$Ni(CO)_4 \xrightarrow{200°C} Ni + 4CO$$

Van arkel method for refining ziroconium 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.

$$Zr + 2I_2 \longrightarrow ZrI_4$$

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

$$ZrI_4 \longrightarrow Zr + 2I_2.$$

(C) Slag formation :

Roasted ore mixed with sand and strongly heated in furnace.

$$\underset{\text{flux}}{FeO + SiO_2} \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

Upper layer containing slag is removed and lower layer contains mostly Cu_2S (98%) with little amount of FeS(2%) is called matte.

(D) Bessemerisation : (Self - reduction)

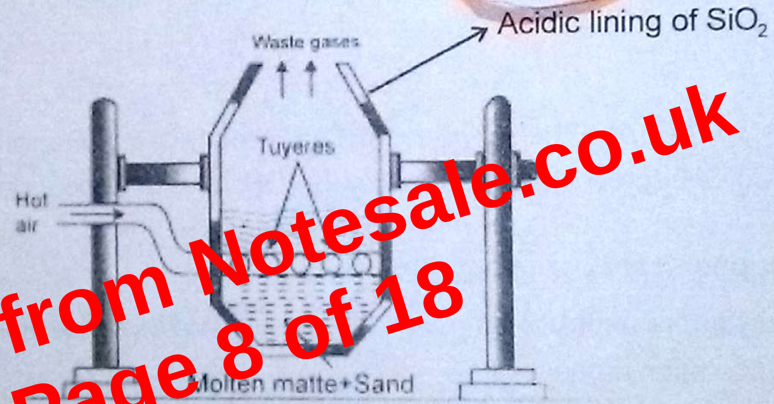
$$2FeS + 3O_2 \xrightarrow{\Delta} \underset{\text{(small amount)}}{2FeO} + 2SO_2$$

$$FeO + SiO_2 \xrightarrow{\text{fuse}} FeSiO_3 \text{ (small amount of slag)}$$

$$2Cu_2S + \underset{\text{(limited air)}}{3O_2} \xrightarrow{\Delta} 2Cu_2O + 2SO_2 \text{ (partial roasting)}$$

$$\underset{\text{(R.A.)}}{Cu_2S} + 2Cu_2O \xrightarrow[\Delta]{\text{high temp.}} \underset{\text{(impure)}}{6Cu} + SO_2 \text{ (self reduction)}$$

Impure copper obtained has blister appearances and therefore called blister copper.



Poling : Molten Cu is stirred with poles of green wood to reduce Cu_2O (copper (I) oxide impurity) into Cu.

Electrolytic refining :

Anode - impure Cu ;

Cathode - Pure Cu ;

Electrolyte $CuSO_4 + H_2SO_4$.

The more electropositive impurities like Zn, Fe, Ni etc. get dissolved in solution and less positive impurities like Ag, Au collect below anode as anode mud.

4. Lead :

Ores : Galena PbS (main ore) ; Anglesite $PbSO_4$; Cerussite $PbCO_3$

Extraction of lead from galena :

Crushing and concentration : The ore is crushed, grinded finely and concentrated by froth floatation process

Roasting : In reverberatory furnace, limited supply of air is passed at moderate temperature.

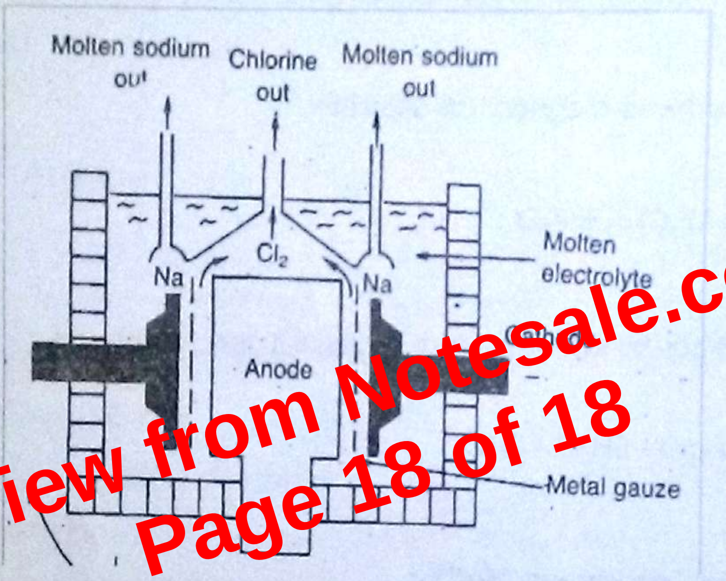
$$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$$

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

10. **Extraction of Sodium : (Down's cell process)**

Sodium metal is isolated by the electrolysis of molten mixture of about 40% NaCl and 60% $CaCl_2$ in a Downs cell method. This mixture melts at about 600°C compared with 803°C for pure NaCl. There are three advantages of lowering the temperature of melt.

1. It lowers the melting point of NaCl.
2. The lower temperature results in a lower vapour pressure for sodium, which is important as sodium vapour ignites in air.
3. At the lower temperature the liberated sodium metal does not dissolve in the melt, because if it dissolved it would short circuit the electrodes and thus prevent further electrolysis.



Downs cell for the production of sodium.

$$2Na^+(\ell) + 2Cl^-(\ell) \xrightarrow{\text{Electrolysis}} 2Na(\ell) + Cl_2\uparrow$$

Reduction at cathode

Oxidation at anode

11. **Potassium :**

Similar electrolytic cell is used to obtain potassium metal by electrolysing fused KCl. However, the cell must be operated at a higher temperature because the melting point of KCl is higher but less than that of NaCl and this results in the vaporization of the liberated potassium, In this modern method, molten KCl is reduced by sodium vapour at 850°C in a large fractionating tower. This gives K metal of 99.5% purity.

$$Na + KCl \rightleftharpoons NaCl + K\ (vapour)$$