Module – 25.4

Process of molten electrolysis of Al

Aluminium:

(a) Occurrence:

In the earth's crust, aluminium is the most abundant (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon). It is never found in the elemental state. The important minerals of Al are given below.

Name of the mineral	Formula
Corundum	Al_2O_3
Diaspore	$Al_2O_3.H_2O$
Bauxite	$Al_2O_3.2H_2O$
Gibbsite	$Al_2O_3.3H_2O$
Cryolite	Na_3AlF_6

(b) Extraction:

For the purpose of extraction of Al, bauxite is by far the important source. From bauxite Al is obtained by electrolysis. For this purpose pure bauxite is necessary. The following steps are used in extraction of aluminum.

(i) Purification of Bauxite(or) Ore concentration
(ii) Electrolytic reduction of alumina
(iii) Refining of aluminium.

(i) Purification of Bauxite:

Bauxite containing iron oxide as impurity is known as **red bauxite**; it is purified either by **Baeyer's process** and by **Hall's process** where as bauxite containing silica as impurity is known as **white bauxite** and is purified by **Serpek's process.**

1. Baeyer's Process:

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution, under pressure (about 35 atm) at 423 K for a few hours in a furnace called autoclave. Alumina reacts with NaOH and forms sodium meta aluminate and the impurities present in that solution are left behind and are removed by filtration.

$$Al_2O_3.2H_2O_{(s)} + 2\ NaOH \rightarrow 2\ NaAlO_{2\ (aq)} + 3\ H_2O_{(l)}$$

The filtered sodium meta Aluminate is diluted with water, then hydrated aluminum oxide is precipitated as aluminum hydroxide.

$$2\ NaAlO_{2\ (aq)} + 4H_2O \rightarrow 2\ NaOH + Al_2O_3.3H_2O$$ **(Hydrated Alumina)**

or

$$2\ Al\ (OH)_3$$

(Aluminum hydroxide)

The precipitate thus obtained is calcined at 1050^0C; the aluminum hydroxide decomposes to alumina, giving of water vapour in the process.

$$2\ Al\ (OH)_{3\ (s)} \xrightarrow{1200^0 C} Al_2O_{3\ (s)} + 3\ H_2O_{(g)} \uparrow$$

2. Hall's Process:

In Hall's process when red bauxite is treated with sodium carbonate aluminum oxide converts into soluble sodium Meta aluminate.

$$Al_2O_3.2H_2O + Na_2CO_3 \rightarrow 2\ NaAlO_2 + CO_2 + 2\ H_2O$$

The extracted sodium meta – Aluminate is separated by filtration, then the solution heated at 500^0c by passing CO_2 to get pure anhydrous aluminum hydroxide.

$$2\ NaAlO_{2\ (aq)} + 3\ H_2O_{(l)} + CO_{2\ (g\ )} \xrightarrow{873\ K} 2\ Al\ (OH)_3\ (s) + Na_2CO_{3\ (aq)}$$

The aluminium hydroxide obtained in this process on heating at 1050^0C gives Alumina.

$$2\ Al(OH)_3 \xrightarrow{1050^0C} Al_2O_3 + 3\ H_2O$$

3. Serpek's process:

In this process, most of the silica of the bauxite is volatilized. Powdered bauxite and coke are mixed and heated in an atmosphere of nitrogen at 1800^0c to get dehydrated alumina.

$$Al_2O_3 + 3\ C + N_2 \xrightarrow{1800^0C} 2\ AlN + 3\ CO$$

$$2\ AlN + 3\ H_2O \rightarrow 2\ Al(OH)_3 + NH_3$$

The Aluminium hydroxide thus obtained is heated to 1050^0c. The Aluminium hydroxide decomposes to Alumina.

$$2\ Al(OH)_3 \xrightarrow{1050^0C} Al_2O_3 + 3\ H_2O$$

(ii) Electrolytic reduction of Alumina:

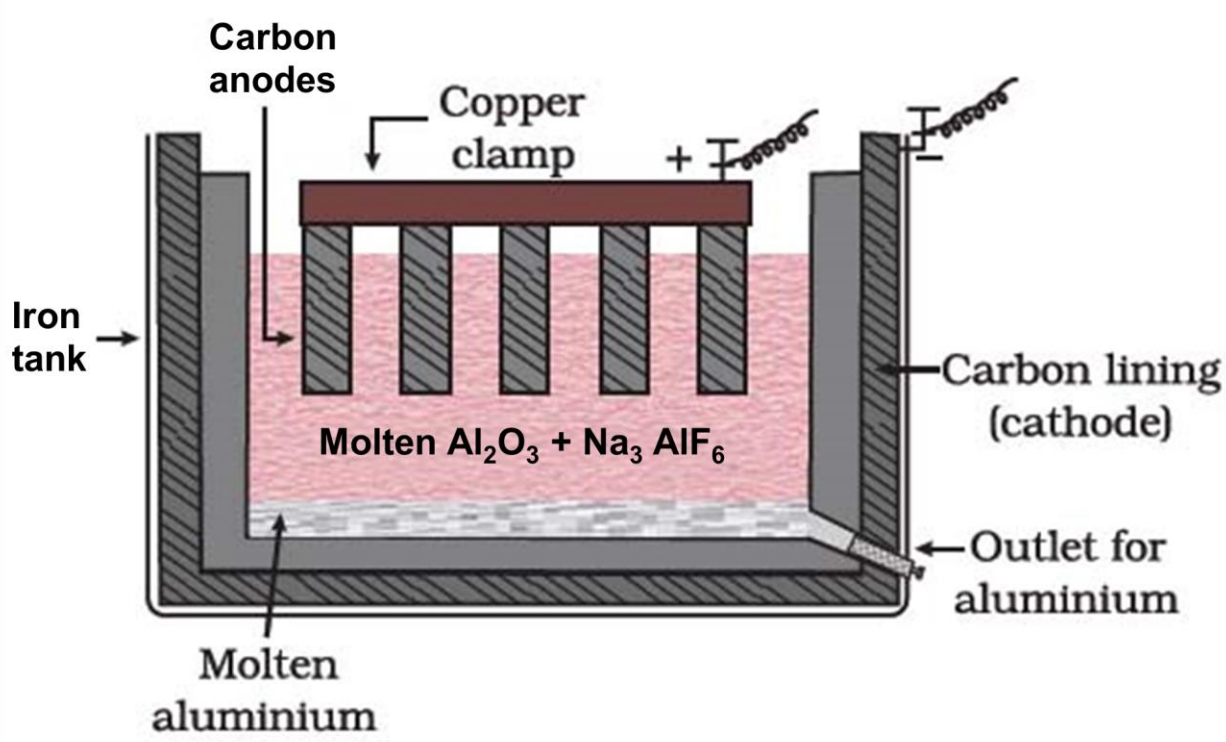
In the metallurgy of aluminium, purified Al_2O_3 obtained from bauxite is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and makes it conductivity. The fused matrix is electrolysed. Electrolysis is carried out in an iron or steel tank. The tank is lined inside with the graphite that acts as cathode. Anode consists of a number of carbon or copper rods. Suspended from the top of the electrolytic cell. The anodes are immersed partially into the electrolyte. The electrolyte consists of a fused mixture of alumina, cryolite and fluorspar. The surface of the electrolyte is covers with powdered coke. This prevents the oxidation of the metal formed in electrolysis.

The following reactions takes place in the electrolytic cell.

$$Na_3AlF_6 \rightarrow 3\ NaF + AlF_3$$

(Cryolite)

$$4\ AlF_3 \rightarrow 4\ Al^{+3} + 12\ F^-$$ (ionization)



Electrolytic cell for the extraction of aluminium

Aluminium ions move towards the cathode (i.e. carbon lining) and they are discharged. Aluminium metal is formed. Fluoride ions are discharged to give fluorine at the anode.

At cathode: $4\ Al^{+3} + 12e^- \rightarrow 4\ Al$

At anode: $12\ F^- \rightarrow 12F + 12e^-$

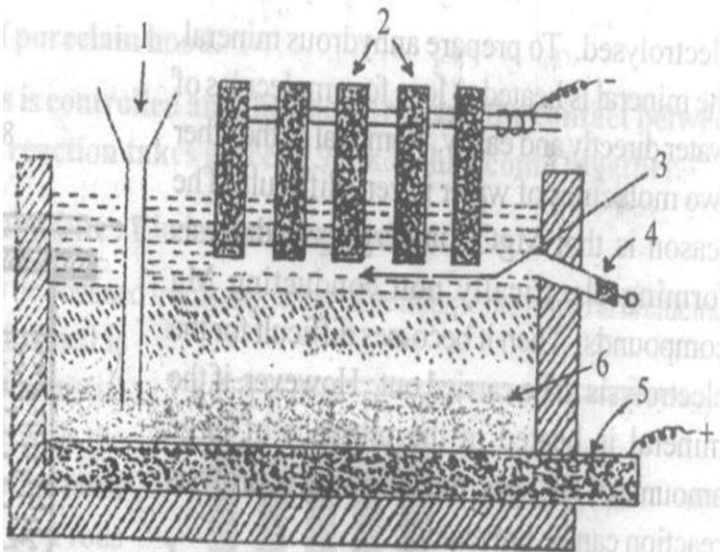
$2\ Al_2O_3 + 12\ F \rightarrow 4\ AlF_3 + 3O_2$

Aluminium produced at the cathode, sinks to the bottom to the bottom of the cell. It is removed from time to time through tapping hole. Fluorine formed at the anode reacts with alumina. Alumina is added at intervals. In this process, 99% pure aluminium is obtained.

(iii) Refining of Aluminium:

Aluminium obtained by the above process contains impurities like Si, Cu, etc. it is further purified by Hoope's electrolytic method.

The electrolytic cell used for refining of aluminium consists of an iron tank lined inside with carbon. It contains three layers of fused masses. These layers differ in their specific gravities. The upper layer is of pure aluminium. A number of graphite rods acts as cathode. They are suspended from the top into the upper layer. The middle layer consists of a fused mixture of fluorides of sodium, barium and aluminium. This layer acts us an electrolyte. The bottom layer contains impure aluminium. The carbon lining of the tank acts as anode. To increase the density of impure. Al layer copper and silicon are added.



1. Impure Al
2. Carbon cathodes
3. Pure Al
4. Opening to remove metal
5. Carbon lining
6. Impure Al

On passing current Aluminium ions from the middle layer, are discharged at the cathode layer (upper layer). Pure Al is deposited in the upper layer. At the same time an equivalent amount of aluminium passes into the middle layer from the bottom layer. 99.89% Al is the result of this process.

Assignment Questions:

1. Describe a method for the refining of impure Al.
2. What is Baeyer's Process? Describe it.

Example set:

1. Bauxite is a mineral of _____

a. Ba
b. B
c. Br
d. Al

Solution: d)

2. Formula of cryolite is _____
   a. Al_2O_3
   b. Na_3AlF_6
   c. $Al_2O_3.H_2O$
   d. $KAlSi_3O_8$

Solution: b)

3. Purification of aluminium by electrolytic refining is known as _____
   a. Hall's process
   b. Baeyer's process
   c. Hall – Heroult process
   d. Hoope's process

Solution: d)

4. Epson salt is _____
   a. $MgSO_4.7H_2O$
   b. $MgSO_4.2H_2O$
   c. $MgSO_4.5H_2O$
   d. $MgSO_4.10H_2O$

Solution: a)

5. Carnalite is a mineral of _____
   a. Be
   b. Mg
   c. Ca
   d. Sr

Solution: b)

6. Write any three minerals of Al?

Solution:

Bauxite ($Al_2O_3.2H_2O$); Corundum (Al_2O_3); Cryolite (Na_3AlF_6)

7. What happens when hydrated aluminium oxide is heated with conc. NaOH solution?

Solution:

Alumina reacts with NaOH and forms sodium meta aluminate

$Al_2O_3.2H_2O_{(s)} + 2\ NaOH_{(aq)} \rightarrow 2\ NaAlO_{2\ (aq)} + 3\ H_2O_{(l)}$

Problem set:

1. In the electrolysis of alumina, cryolite is added to _____
   a. Decrease the melting point of alumina
   b. Increase the electrical conductivity
   c. Both a and b
   d. Remove impurities from alumina

Solution: c)

2. Red Bauxite contains _____ as major impurity which can be purified _____ process.
   a. Iron oxide, Baeyer's or Hall's
   b. Iron oxide, serpek's
   c. Sand, Serpek's
   d. Sand, Hall's

Solution: a)

3. Method used to remove silica impurities from the Bauxite.
   a. Hall's method
   b. Baeyer's method

c. Serpek's method
d. Hoope's method

Solution: c)

4. How is bauxite purified by Serpek's process?

Solution:

By Serpek's process:

In this process, most of the silica of the bauxite is volatilized. Powdered bauxite and coke are mixed and present in heated in a nitrogen atmosphere at 1800^0C to get dehydrated aluminum hydroxide.

$$Al_2O_3 + 3\,C + N_2 \xrightarrow{1800^0C} 2\,AlN + 3\,CO$$

$$2\,AlN + 3\,H_2O \rightarrow 2\,Al(OH)_3 + NH_3$$

The Aluminium hydroxide thus obtained is heated to 1050^0c (calcined) the Aluminium hydroxide decomposes to Alumina, giving of water vapour in this process.

$$2\,Al(OH)_3 \xrightarrow{1200^0C} Al_2O_3 + 3\,H_2O$$

5. Write the equations for the chemical reactions that take place in the electrolysis of fused alumina?

Solution:

The following reactions take place in the electrolytic cell.

$Na_3AlF_6 \rightarrow 3\,NaF + AlF_3$

(Cryolite)

$4\,AlF_3 \rightarrow 4\,Al^{+3} + 12\,F^-$

At cathode: $4\,Al^{+3} + 12e^- \rightarrow 4\,Al$

At anode: $12\,F^- \rightarrow 12F + 12e^-$

$2\,Al_2O_3 + 12\,F \rightarrow 4\,AlF_3 + 3O_2$

Exercise questions:

1. What is the role of cryolite in the metallurgy of aluminium?
2. What is the role of graphite rod in the electrometallurgy of aluminium?
3. Outline the principles of refining of metals by the Electrolytic refining methods:
4. Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese etc. Explain why?

Solutions to exercise questions:

1. Cryolite (Na_3AlF_6) has two roles in the metallurgy of aluminium: They are
   a. To decrease the melting point of the mixture from 2323 K to 1140 K.
   b. To increase the electrical conductivity of Al_2O_3.

2. In the electrometallurgy of aluminium, a fused mixture of purified alumina (Al_2O_3), cryolite (Na_3AlF_6) and fluorspar (CaF_2) is electrolysed. In this electrolysis, graphite is used as the anode and graphite-lined iron is used as the cathode. During the electrolysis, Al is deposited at the cathode, while CO and CO_2 are liberated at the anode, according to the following equations.

   Cathode: $Al^{3}_{(melt)} + 3e^{-} \rightarrow Al_{(i)}$

   Anode: $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^{-}$

   $$C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_{2(g)} + 4e^{-}$$

If a metal is used instead of graphite as the anode, then O_2 will be liberated. This will not only oxidise the metal of the electrode, but also convert some of the Al liberated at the cathode back into Al_2O_3. Hence, graphite is used for preventing the formation of O_2 at the anode. Moreover, graphite is better and is cheaper than other metals.

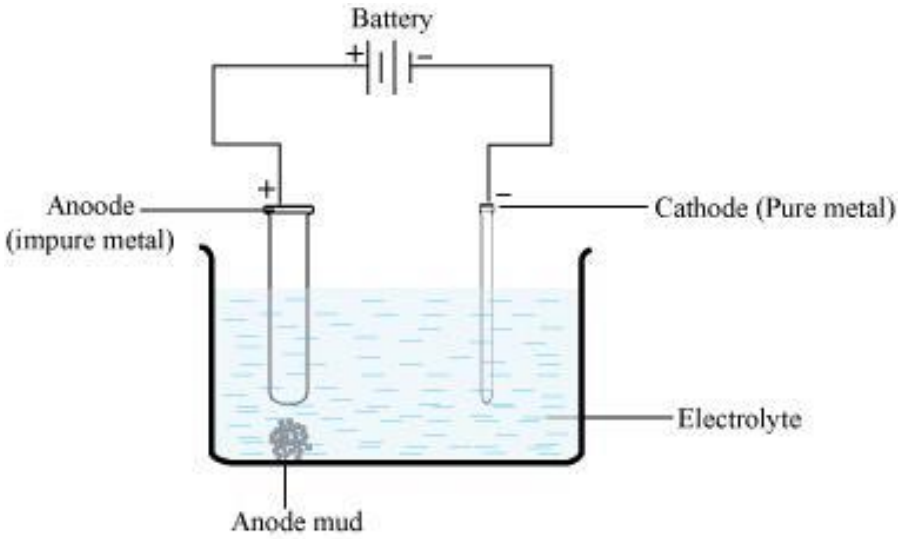
3. **Electrolytic refining:**

Electrolytic refining is the process of refining impure metals by using electrolysis principle. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the metal to be refined,

is taken as the electrolyte. When an electric current is passed, metal ions from the electrolyte are deposited at the cathode as pure metal. The impure metal from the anode dissolves into the electrolyte in the form of ions. The impurities present in the impure metal gets collected below the anode. This is known as anode mud.

Anode: $M \rightarrow M^{n+} + ne^-$ (Anode material dissolves)

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



4. Aluminium has great affinity for oxygen. It acts as a reducing agent when the metal having highest melting point is to be extracted from its oxide.

   Ex: $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$