Metallurgy of Aluminium

Ores of Al

The natural occurring substance from which a metal or other mineral is extracted is called ore.

Metallurgy is the complex process because some metals are found in combine form. We need to separate the main metal from ore through series of chemical reactions. e.g. Bauxite is a ore of Aluminum which contains 50-70% aluminum oxide. Al, K, Na, etc are so reactive and they can't be found in Free State in nature. They can be found in oxide form.

Extraction of metal from ore

This consist on following stages

1. Concentration or dressing
   In this stage the impurities are separated as much as possible like rock, clay and sand etc.
2. Extraction of crude metals
   In different metals this method is different based on metal reactivity. From this method crude metal is obtained.
3. Refining or Purification
   In this stage crude metal is refined.

Metallurgy of Aluminum

Introduction:

Aluminum is the third most abundant element on the earth's crust. It was discovered by Davy in 1805.It has an atomic number 13.It belongs to period 3 and group 13(IIIA).

Hall in the USA and P. Heroult in France obtained aluminum by electrolysis of alumina dissolved in molten cryolite. This Hall and Heroult method remained most convenient and economic production method of aluminum throughout the world. Aluminum (in oxide form) is contained in 15% of the earth's crust.

Physical Properties of aluminum

Aluminum is silvery white in color. It melts at1220.576 Fahrenheit and boils at 4472.33. Its atomic radius is 143.1pm.It is one of the most ductile and malleable metals. Aluminum is non magnetic.

Chemical Properties of Aluminum

When aluminum reacts with oxygen it forms an oxide skin called aluminum oxide. This skin helps to protect aluminum from corrosion. Aluminum catches fire easily if exposed to flame when it is in powdered it is recitative with both acids and alkalis.

Sources of Aluminum

Most common:

- Gibbsite ($Al_2O_3.3H_2O$) ($Al_2O_3.45.4\%$),
- Diaspore ($Al_2O_3.H_2O$) ($Al_2O_3.85.4\%$)

Bauxite is the mixture of these two, with various amounts of Fe_2O_3, TiO_2 and SiO_2.

Extraction of Aluminum

The Aluminum oxide is very stable. The carbothermic reduction of aluminum oxide has not been adopted because

1. It required a high temperature (Above 2000°C)
2. At that temp Aluminum carbide is formed
3. The refractory required, for such high temp is readily available and expensive.

Universally adopted Process is **electrolysis** of pure Al_2O_3 dissolved in cryolite ($3NaF.AlF_3$). Cryolite can be synthesized and it is a rear example of an oxide dissolved in a halide. Electrolysis is energy consuming process it also uses graphite electrodes.

Processes

Extraction of Aluminum can be done by following process.

1. ## Bayer Process
   In this process high purity Alumina is produced. Bauxite is leached by Sodium hydroxide from
   Soluble sodium aluminates under high pressure (25atm) and temperature (220C) , from which $Al(OH)_3$ is obtained as precipitates. From $Al(OH)_3$ alumina is obtained by calcinations.

Initially, bauxite is obtained by crushing the mines .This bauxite is ground to a very fine size and silica is separated from bauxite. By comminuting, alumina can be enriched in the coarser fraction.

The coarser fractions are ground with caustic soda to obtain slurry in a ball mill. This slurry is fed into an autoclave at 220°C and 25atm pressure.

The alumina, in the bauxite, is dissolved in caustic soda as:

$$Al_2O_3.H_2O + 2NaOH = 2NaAlO_2 + H_2O$$

$$Al_2O_3.3H_2O + 2NaOH = 2NaAlO_2 + 4H_2O$$

The impurities like in bauxite like Fe_2O_3 and Sio_2 leave as suspended solid in solution. The dissolution of alumina monohydrate required temp of 230°C for three hours. And for alumina trihydrate required temp of 180°C for one hour.

Since the bauxite is the mixture of monohydrate and trihydrate, so temp required 1680-220°C for 2.5 hours and 86-88% alumina in the bauxite goes into the solution. At this temp, a high pressure 5-25 atm is required to retain water in liquid state. Then liquid is cooled below 100°C and the settling of red mud is increased by adding starch. The remaining red mud in the liquid is removed by washing with hot water than liquid is filtered and filtrate obtained is clear solution of sodium aluminates.

The remaining left behind after filtration have ferric hydroxide, silica and non dissolved alumina in the hot liquid heat is removed by heat exchanger for conservation and for cooling the liquid below the critical temp required for alumina precipitation. Then aluminum hydroxide is added to create nuclei to speed up the precipitation of $Al(OH)_3$. This precipitate is separated from liquid in the thickener, and the product is calcined in a rotary kiln to produced anhydrous alumina. Depending on calcinations temp, resultant Al_2O_3 is a

lose hydroscopic ɣ Al_2O3 at 800˚C or more dense αAl_2O_3 at 1200˚C is produced but generally the product is the mixture of both components due slow rate of transformation

$$2NaAlO_2 + 4H_2O = 2\ Al\ (OH)_3 + 2NaOH$$

$$2Al\ (OH)_3 = Al_2O_3 + 3H_2O$$
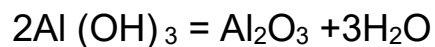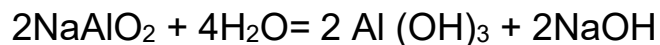
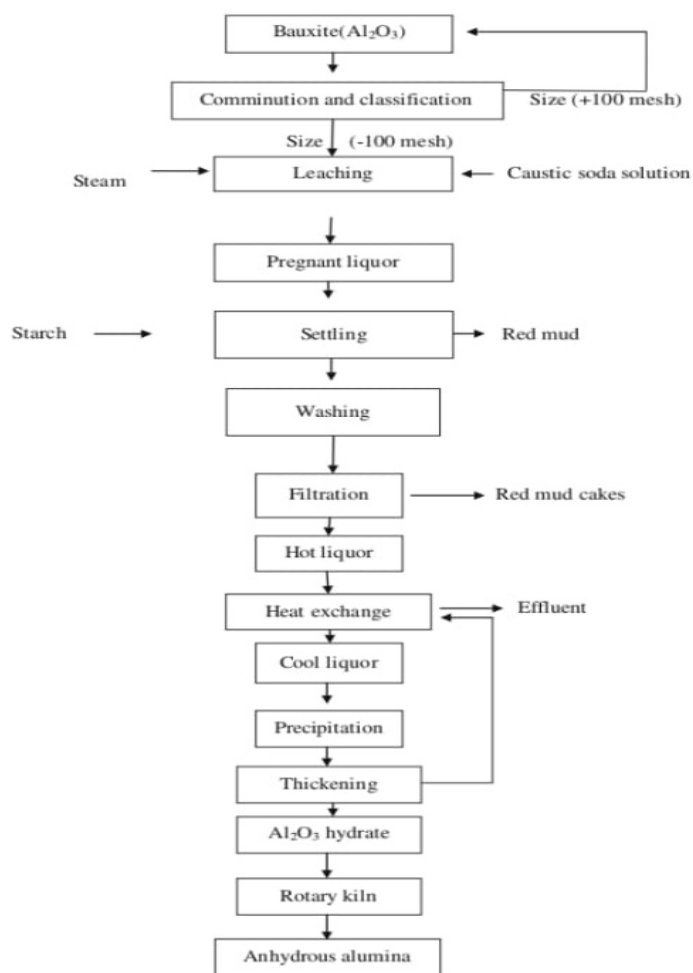8.3 Extraction of Aluminium   113

Fig. 8.1 Flow sheet of Bayer process

Factors effecting on Bayer Process

The effect of various factors on efficiency of Bayer process is as followed

1. The finer the bauxite, the alumina will dissolve in batter way in the leach liquid.
2. Wet grinding is better than dry grinding, and it required less time for dissolution
3. Dissolution is increased by increasing temp above 100°C water would be evaporated, high pressure up to 25 atm is required to attain 220°C
4. Low temp is required as below that limit aluminum hydroxide is precipitated leading to a loss of alumina
5. The sensible heat gain from hot liquid is used for steam in dissolution
6. The total amount of alumina in solution is not permitted to precipitate because this lead to simultaneous precipitation of dissolved silica so the precipitation is kept incomplete, the remaining solution is recirculated to the dissolution stage
7. For the efficient calcinations of alumina, the rotary kiln should gain a high temp 1400°C. The decomposition of Al (OH)$_3$ produces Al$_2$O$_3$.H$_2$0 and Al$_2$O$_3$.3H$_2$0. For the dehydration of monohydrate and trihydrate mini temp as 1200°C and 800°C respectively is required.

Hall- Heroult Process

Heroult in France and Hall in the USA independently introduced a process for the commercial production of aluminium in 1886.

The electrolytic decomposition of alumina dissolved in a liquid bath of cryolite is the base of this process.

The cheap electric power is the primary requirement for the Hall-Heroult process, in which high purity alumina, ashless carbon electrodes and cryolite is required

In an electrolytic cell the electrolysis of aluminium from alumina is done.

The cell is made up of 5m long, 2m wide and 1 m deep rectangular refractory lined steel container.

The conducting bottom of the container acts as cathode which have refractory bricks   carbon bonded with tar binder. Iron bar and iron plate are embedded in the carbon used as good conductor to form cathode.

Anodes have one of two forms: firstly, the anode may be carbon electrodes and replaced from time to time. A copper is embedded in the bar for contact with the cell bar.

The complement of one cell is formed by 24 anodes.

Its average life is 8–10 days. Secondly, the continuous electrodes formed by continuous carbonaceous paste (hot mixture of 70% petroleum and 30% pitch as binder) into the steel moulds.

The carbonaceous paste is baked itself in the cell during electrolysis by heating attained from the resistance offered to the pathway of the electric current, it acts as anode.

The lining cathode and the baked carbon anode must be strong (250–300 kg/cm2 of strength) and density (< 25% porosity).

Iron pins attached to the casing aluminum bus bars help in electrical contact and to carry the weight of the electrodes.

When the electrode is consumed and it lowered into the electrolyte then the sheet of aluminium casing melts and it joints the electrolyzed metal in the cell bottom.
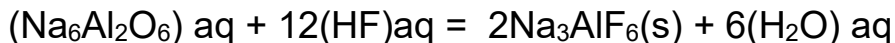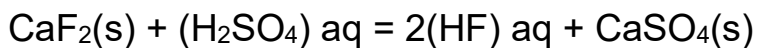
For the collection of molten aluminium metal a tap hole is located on the furnace bottom.

The bath density must be less than the liquid aluminum, otherwise the liberated metal will float and it will upset cell operation.

Molten aluminum is collected at the bottom, due to high density (2340 kg/m3) than that of the electrolyte (2030 kg/m3).

As alumina is not an ionic compound, so few ionic melts are capable to dissolve it to any proper extent. However, cryolite (3NaF.AlF3), which is a natural mineral, it can dissolve up to 15% alumina at temperature 1000°C.

Cryolite is synthesized by passing hydrogen fluoride (HF) through sodium aluminates' ($Na_6Al_2O_6$) solution, the hydrogen fluoride (HF) is produced from CaF2.

$$CaF_2(s) + (H_2SO_4) \ aq = 2(HF) \ aq + CaSO_4(s)$$

$$(Na_6Al_2O_6) \ aq + 12(HF)aq = 2Na_3AlF_6(s) + 6(H_2O) \ aq$$

In the cryolite bath small amounts of CaF_2 and NaF are added to enhance its conductivity, and these also　improve the recovery of metal.

Cryolite melts at high temperature 990°C; at this temperature cryolite takes 10% of its weight of alumina.

Density of molten cryolite is approximately 2100 kg/m^3 at 1000°C density of Al_2O_3 IS 3960kg/m^3 as it sinks at the bottom of the cell.

During electrolysis in presence of about 10% CaF_2, 80% cryolite, 5% Al_2O_3, and a small amount of NaF the aluminium (density 2340 kg/m3) is liberate, and it is heavier than the bath and collected at the bottom.

In this way, the aluminium metal is saved against atmospheric oxidation.

The density is a factor which limits the concentration of Al_2O_3 in the bath; with higher amount of Al_2O_3 density also increases at high rate.

The sinking of aluminium is rendered more difficult.

Electrolyte depth is maintained at about 0.25 m. During function, the cell is filled with cryolite and the anode is dipped into that Current is passed through the cell until the cryolite melts at 990°C.

When the bath gains the molten state, then alumina is charged to the cell.

The alumina decomposes to aluminum and oxygen in an endothermic reaction during this reaction necessary heat is supplied by the resistance of both the electrodes and the electrolyte.

$$2Al_2O_3 = 4Al + 3O_2 = 838,683 J/mol \text{ of } Al_2O_3$$
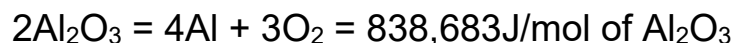
This oxygen reacts with carbon to form CO and CO2 gases in anode. The agitation in bath takes place due to evolution of CO and CO2 gases, and by magnetic stirring due to current flow from anode to cathode through the bath.

The agitation maintains fresh additions of alumina in suspension long enough. If the alumina of the bath normally 5– 10% decreases below 2%, then between the anode and the bath the normal contact is interrupted by gas film which enhance the resistance which increases voltage from 5–6 V to as much as 40–50 V.

At anode surface Fluorine gas is deposited where it forms a gas film and this film is electrically insulating, cause a rise in the voltage.

Then the current is carried by arcing between the carbon anode and the electrolyte. Due to which normal operation is hampered. This effect is called anode effect.

By adding sufficient amount alumina to the bath the voltage gains its normal value. When alumina is added in molten cryolite the ions are present as:
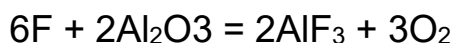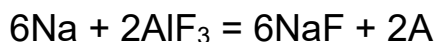
In solute: Al^{3+}, O^{2-}

In solvent: Na^+, Al^{3+}, $AlF_6{}^{3-}$, F^-.

Only the oxygen ions (O^{2-}) are the only foreign ions to the solvent and they may react with Al^{3+} to form AlO^+ and AlO_2^- in the melt. Further Al_2O_3 may go into solution in the form of AlO^+ and AlO_2^-. During electrolysis, several reactions take place simultaneously by involving all the ions in the melt.
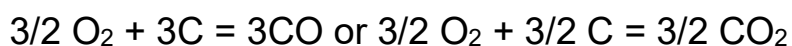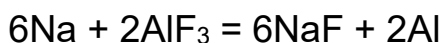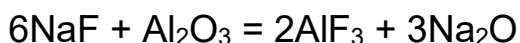
$$Na_3AlF_6 = NaAlF_4 + 2NaF$$

$$NaAlF_4 = NaF + AlF_3$$

The NaF produced starts a number of reactions that are indicated by the following two theories.

Theory 1: The NaF is dissociated into F and Na:

$$6NaF = 6Na + 6F$$
$$6Na + 2AlF_3 = 6NaF + 2A$$
$$6F + 2Al_2O3 = 2AlF_3 + 3O_2$$
$$3O_2 + 6C = 6CO \text{ or } 3O_2 + 3C = 3CO_2$$

Theory 2: The NaF reacts with Al_2O_3 to form Na_2O:

$$6NaF + Al_2O_3 = 2AlF_3 + 3Na_2O$$
$$3Na_2O = 6Na + 3/2\ O_2$$
$$6Na + 2AlF_3 = 6NaF + 2Al$$
$$3/2\ O_2 + 3C = 3CO \text{ or } 3/2\ O_2 + 3/2\ C = 3/2\ CO_2$$

The upper two theories show the constant presence of sodium vapor and fluorine above cryolite bath to the decomposition of NaF.

It is also noted that the depletion of alumina or the lowering of its activity enhance the formation of fluorine or NaF. A more generation of fluorine causes the anode effect, which resists normal operation

Factors effecting electrolysis

The following factors affect the electrolysis of alumina are as follows:

1. The bath temperature is very important factor. Increase in temperature decreases the current efficiency. For every 4°C rise in the bath temperature (above the normal 970°C), the current efficiency decreases by 1% because with increase in temperature number of side reactions increasea and the dissolution of the metal increases in the bath.

2. With increase in the current density the current efficiency increases.So the current density is maintained at a very high value.

3. The lower the density of the bath, the higher the rate of separation of the metal extracted from the bath. The density is lowered by a high AlF_3/NaF ratio; a ratio of slightly less than 3 is taken optimum. When the quantity of AlF_3 is greater than NaF, the conductivity of the bath decreases and the solubility of alumina reduce, and a large volume of fluorine is produced. But the higher the NaF content lower the current efficiency because the concentration of sodium ions increases and the sodium deposition on the cathode. The deposition of sodium directly lowers the current efficiency.

4. The interpolar distance also effect the current efficiency. The Inter polar distance is the distance from the anode bottom to the top of the molten

bath. The current efficiency increases with inter- polar distance, When the distance is about 0.65 m then current efficiency is maximum (90%).

5. By controlling the addition of alumina the cell efficiency is improved. When the AlO_3 is 4% in the bath then current efficiency is minimum. When values are lower or higher than 4% the current efficiency increases. Current efficiency has empirical relations with operating variables as shown:

CE = $254.92 - 1.7C_{A1203} + 0.39C^2_{Al203} + 0.45AlF_3 + 0.055X^2_{AlF3} + 0.3C_{CaF2} - 0.23T +$

129/ (D+1) +25i

T=Temperature of the cell   D=Inter electrode distance

I=anode current density Ca_{Al203}=Wt% of Al_2O_3 C_{CaF2}=Wt% of CaF_2

X_{AlF3}=mol fraction of AlF_3

Refining of Aluminium

The pure aluminium metal produced by the Hall-Heroult process is about 99.5%, this is sufficient for most alloying purposes. But, for electrical applications and for canning, a higher degree of purity is required. To gain high purity, an electrolytic method is used which is also known as the three layer process in which the graphite electrode is used as cathode and carbon bottom are used as anode.

During refining electrolysis's takes place in a cell in which the anode is placed at the bottom. The current travelling through the bath is collected at the top by graphite electrodes. This method depends on the adjustment of

the specific gravity of the electrolyte for proper operation so that it is lighter than a copper-aluminium alloy of anode, but it is heavier than pure aluminium

A dense electrolyte (which consists of 36% aluminium fluoride, 30% cryolite, 18% barium fluoride, and 16% calcium fluoride) forms the middle layer (density is 2800 kg/m3). The impure metal is alloyed with copper (28–30% Cu), and this heavy alloy (density is 4500 kg/m3) forms the layer of bottom. The purified aluminium (99.99%, density is 2300 kg/m3) flows upward during electrolysis and it form the top layer. The temperature 950˚C is required for electrolysis. Magnesite refractory acts as insulating wall.

Refining reactions are shown as follows:

At anode: $Al \rightleftharpoons Al^{3+} +3e$

At cathode: $Al^{3+} +3e \quad Al$
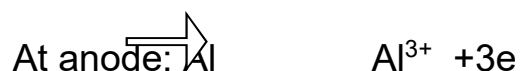
At the anode impure aluminium is dissolved and forms Al^{3+} ions, then aluminium ions (i.e. $Al3+$) in the pure form are deposited at the cathode.

Commercial aluminium is poured in a molten condition into the well connected with the anode alloy metal in the cell bottom. Current from this layer passes pure aluminum through the electrolyte and it float on the top layer from where it is taken out.

The remaining impurities in the bottom gradually build up alloy layer and having a relatively low solubility is crystallize out in the later stage. These impurities mainly consist of iron, silicon, zinc and copper with aluminium. The consumption of the electrolyte and graphite electrode each is equivalent to about 6% of the aluminium metal produced. This method is also practiced for the refining of aluminum scrap without magnesium. If the impure metal

contains magnesium which come from Al–Mg scrap then this process will be ineffective, due to magnesium reacting with the electrolyte.

Applications

After copper, aluminium metal is considered the most important non-ferrous metal.Aluminium is a good conductor of heat and electricity, and it is also less expensive than copper, nowadays aluminum is replacing the copper in electrical applications.

Aluminium is gradually replacing the copper in the power transmission lines. A conductor made of aluminium surround a core of steel wires with a high tensile strength is used as an conductor.The core compensates for the low strength of aluminium. Aluminum strips or foils interleaved with insulators are used for transformer winding.

 Aluminium it is used for extrusion of vessels and containers due to its ductility. Pure grade aluminium is used for kitchenware, chemical and food processing due to its corrosion resistance and non-toxic properties. Aluminium explains its use as roofing and thermal insulation either as metal foil or aluminium paint. Aluminium acts as deoxidizing agent to remove oxygen in liquid steel in steel making.