Metallurgy of Aluminium

Metallurgy can be **defined** in the following ways : 1-Metallurgy is a domain of materials science and engineering that **studies the physical and chemical behavior of metallic elements**, their inter metallic compounds, their alloys(mixtures).

2-Metallurgy is defined as a process that is used for the **extraction of metals** in their pure form.Metallurgy deals with the process of purification of metals and the formation of alloys.

Aluminium :

Aluminium (Al), a lightweight, silvery-white metal of Group IIIA of the periodic table. Aluminum is the most abundant metallic element in Earth's crust and the most widely used metal (after iron). Because of its chemical activity, aluminum never occurs in the metallic form in nature, but its compounds are present in almost all rocks, vegetation, and animals. Aluminum is concentrated in the outer16 km of Earth's crust, of which it constitutes about 8 percent by weight. The name aluminum is derived from the Latin word alumem, used to describe potash alum (or aluminum potassium sulfate, $KAl(SO_4)_2 \cdot 12H_2O$).

General properties and occurrence :

Aluminum occurs in igneous rocks mostly as **aluminosilicates, bauxite** and iron-rich laterite. Bauxite is the principal aluminum ore (The most common aluminium minerals are alumina trihydrates as gibbsite ($Al_2O_3.3H_2O$) and alumina monohydrates as diaspore ($Al_2O_3.H_2O$). The theoretical Al_2O_3 present in gibbsite is 65.4%, and in diaspore is 85.4%. Bauxite is a mixture of these two minerals). Bauxite contains varying amounts of impurities such as Fe_2O_3, TiO_2 and SiO_2. Crystalline aluminum oxide is mined as a natural polish or in its solid varieties as rubies and s**apphires. Aluminum is present in other gemstones as well,**such as topaz, garnet, and chrysoberyl. Other aluminum minerals like **alunite and cryolite** also have commercial importance.

Physical properties :

Pure aluminum (99.9 %) is quite soft and weak; commercial aluminum (99 -99.6%) with small amounts of silicon and iron is hard and strong. Ductile and highly malleable. The metal is only about one-third as dense as compaired to iron or copper. Aluminum is highly corrosion-resistant, because in air a hard, tough oxide film forms on its surface.Aluminum is an excellent conductor of heat and electricity. It crystallizes in the face-centred cubic structure. All natural aluminum is the isotope of aluminum-27. Atomic weight of aluminium is 26.97, melting point is 660°C and boiling point is 1800°C.At room temperature, aluminium has a specific gravity of 2.7. The tensile strength of commercial aluminium is low, ranging from 6.3–14.2 kg/mm2 according to the amount of cold working. The modulus of elasticity of aluminium is approximately one-third of that of steel, the elastic deflection of aluminium is three times that of steel.Purer grades of aluminium are known as super-purity aluminium, and contain not less than 99.99% Al. The super-pure aluminium is softer, more ductile, heats more efficiently, and possesses higher thermal and electrical conductivities and greater resistance to corrosion than the commercial metal.

Chemical properties :

Aluminum is slowly attacked by most dilute acids and quickly dissolves in concentrated hydrochloric acid. Concentrated nitric acidr, can be shipped in aluminum tank cars because it makes the metal passive. Even the purest aluminum is severly attacked by bases such as sodium and potassium hydroxide to yield hydrogen and the aluminate ion. Because of its massive affinity for oxygen, finely divided aluminum, if ignited, will burn to form carbon monoxide or carbon dioxide with the formation of aluminum oxide and carbide, but at temperatures that are very high aluminum is inert to sulfur.

Extraction metallurgy of aluminum:

Aluminium is industrially a very important metal but in order to be used in the ways that are industrially useful, we have to obtain it in pure form from its ores. The methods employed in the extraction of metals to be used industrially are called as extraction metallurgy.

Metallic aluminum is not found in nature; it occurs in the form of hydrated oxides or silicates (clays). The principal ore from which aluminum is extracted is called bauxite.The major impurities include iron oxides, silicon dioxide and titanium dioxide.

Aluminum is too much reactive to extract it from its ore using carbon reduction. The temperatures needed are too high. Instead, it is extracted by electrolysis. The ore is first converted into pure aluminum oxide by the Bayer Process, and then it is electrolyzed in solution in molten cryolite. The aluminum oxide has too high melting point to get electrolyzed on its own.

The Bayer Process(Step 1)

1.Reaction with sodium hydroxide solution

Crushed bauxite is mixed with mildly concentrated sodium hydroxide solution. The concentration, temperature and pressure used is dependent basically upon the source of the bauxite. Temperatures are usually from 140°C to 240°C; pressures can be up to about 35 atm. High pressures are important to keep the water in the sodium hydroxide solution liquid at temperatures above 100°C. The greater the temperature, the greater the pressure needed. When treated with hot concentrated sodium hydroxide solution, aluminum oxide reacts to give a solution of sodium tetrahydroxoaluminate.

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$

The impurities in the bauxite remain as solids. For example, the other metal oxides present do not react with the sodium hydroxide solution and so remain unchanged. (Some of the silicon dioxide gives reaction, but goes on to form a sodium aluminosilicate which precipitates out). All of these solids are taken out from the sodium tetrahydroxoaluminate solution by filtration. They form a "red mud" which is stored in huge lagoons.

Precipitation of aluminum hydroxide

The sodium tetrahydroxoaluminate solution is cooled, and treated with some already present produced aluminum hydroxide. This provides something for the new aluminum hydroxide to precipitate around.

$NaAl(OH)_4 \text{------>} Al(OH)_3 + NaOH$

Formation of pure aluminum oxide

Aluminum oxide (alumina) is made by heating the aluminum hydroxide to a temperature of about 1100 - 1200°C.

$2Al(OH)_3 \text{------>} Al_2O_3 + 3H_2O$

Waste Products of Bayer's Process

Red mud is a waste product that is produced in the digestion of bauxite with sodium hydroxide. It has high calcium and sodium hydroxide concentration with a complex chemical composition, and accordingly is very caustic and a source of pollution. The amount of red mud produced is considerable, and this has made scientists and refiners to seek uses for it. One such use is in ceramic production. Red mud dries into a fine powder that has iron, aluminum, calcium and sodium. It becomes a health risk when the plants use these waste to produce aluminum oxides.

Factors affecting the Bayer's process

The effect of various factors on the efficiency of the Bayer process is as follows:

- For the better dissolution of alumina in the leach liquid the bauxite should be finely powered
- Wet grinding is more efficient than dry grinding, and also quicker.
  Dissolution is accelerated by increasing temperatures; above 100°C water would be evaporated, hence high pressures up to 25 atmospheres are applied to attain a temperature up to 220°c.
- There is a lower limit to the temperatures. Below that limit, aluminium hydroxide may precipitate, leading to a loss of alumina.
  The sensible heat, collected from hot liquid, is used for producing steam for dissolution.
- The entire amount of alumina in solution is not allowed to precipitate because this may lead to the simultaneous precipitation of dissolved silica. Therefore, the precipitation is deliberately kept incomplete; the residual solution is recirculated to the dissolution stage.

- For the efficient calcinations of alumina, the rotary kiln should be able to attain temperature as high as 1400°C. The decomposition of Al(OH)3 producesbAl2O3.H2O and Al2O3.3H2O (water is chemically bound). The minimum temperatures required for the dehydration of the monohydrate and the trihydrate are 1200°C and 800°C respectively.

HALL HEROULT'S PROCESS(Step 2)

Process is done in an electrolytic cell.it has a steel contoner bottom acting as cathode, it has carbon bricks mixed with iron plates. The anode may be a carbon rod to which copper wires are connected or conduction with the cell. Or it can be the continuous electrodes by continuous feeding carbonaceous paste (hot mixture of 70% petroleum or pitch coke and 30% pitch as binder) into the steel moulds. The carbonaceous paste is baked in the cell itself during electrolysis by the heat resulting from the resistance offered to the passage of the electric current, and acts as the anode. Electrical contact is established by rows of iron pins attached to the casing and to aluminium bus bars which also help to carry the weight of the electrode. A hike is at the bottom for collection of molten aluminium. The density of the bath must be less then that if aluminium for proper libration.

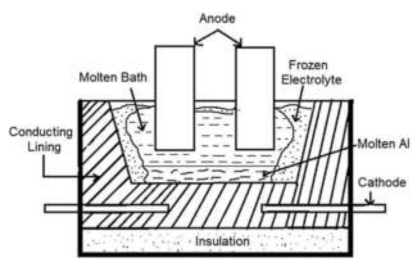

Fig. 8.2 Hall-Heroult process for aluminium production

Small amounts of CaF2 and NaF are added to the cryolite bath to enhance its conductivity and to improve the metal recovery. Cryolite melts at 990°C, at which temperature it will take up to 10% of its weight of alumina. At 1000°C, the density of the molten cryolite is approximately 2100 kg/m3 and that of Al2O3 is 3960 kg/m3 which sink at the bottom of the cell. When the bath containing about 10% CaF2, 80% cryolite, 5% Al2O3, and a small amount of NaF is electrolyzed, the aluminium (density 2340 kg/m3) is liberated which is heavier than the bath and collected at the bottom of the bath. In this way, the aluminium metal is protected against atmospheric oxidation.

During operation, the cell is filled with cryolite and the anode is lowered into that. Current is passed through the cell until the cryolite (melting point 990°C) melts. When the bath attains the molten state, then only alumina is charged to the cell. The alumina decomposes to aluminum and oxygen, which is an endothermic reaction, necessary heat is supplied by the resistance offered by both the electrodes and the electrolyte.

$2Al_2O_3 = 4Al + 3O_2, \Delta H° = 838; 683$ *J/mol of Al2O3*

This oxygen reacts with carbon in anode to form CO and CO_2 gases. The agitation of the bath takes place due to evolution of CO and CO_2 gases; as well as magnetic stirring due to the current flowing through the bath from anode to cathode. The agitation help maintain fresh additions of alumina in suspension long enough for dissolution in the electrolyte. If the alumina content of the bath (normally 5–10%) decreases below 2%, then normal contact between the anode and the bath is interrupted by a gas film which increases the resistance which causes the voltage to rise from 5–6 V to as much as 40–50 V. Fluorine gas is deposited at the anode

The electrode reactions

Although the electrolytic reaction of the Hall-Hetoult process is highly complex and complicated, but for the sake of convince I have written the simplified and summarized form of reaction:

Cathode: $Al^{3+} + 3\ e^- \rightarrow Al$

Anode: $O^{2-} + C \rightarrow CO + 2\ e^-$

Overall: $Al_2O_3 + 3\ C \rightarrow 2\ Al + 3\ CO$

In reality, much more CO_2 is formed at the anode than CO:

$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$

Pure cryolite has a melting point of 1009±1 °C. With a small percentage of alumina dissolved in it, its melting point drops to about 1000 °C. Besides having a relatively low melting point, cryolite is used as an electrolyte because, among other things, it also dissolves alumina well, conducts electricity, dissociates electrolytically at higher voltage than alumina, and also has a lower density than aluminum at the temperatures required by the electrolysis.

Voltage required for the process

The mixture is electrolysed by passing a low voltage (under 5 V) direct current at 100–300 kA through it. This causes liquid aluminium metal to be deposited at the cathode, while the oxygen from the alumina combines with carbon from the anode to produce mostly carbon dioxide.The theoretical minimum energy requirement for this process is 6.23 kWh/(kg of Al), but the process commonly requires 15.37 kWh. .

Efficiency of Hall Heroult Process :

The Hall–Heroult process produces aluminium with a purity of about 99%. Further purification can be done by using the Hoopes process. This process consists of the electrolysis of molten aluminium with a Na, barium, and Al- fluoride electrolyte. The product aluminium has a purity of 99.99%.Electric power represents about 20 to 40% of the cost of producing aluminium, depending on the location of the smelter. Aluminium production uses roughly 5% of electricity generated in the United States. Because of this, alternatives to the Hall–Héroult process have been researched, but nothing has turned out to be economically feasible.

Factors Affecting Electrolysis

- increased temperature decreases the current efficiency. For every 4°C rise in the bath temperature (above the normal 970°C), the current efficiency falls by 1% because the higher the temperature, the more the number of side reactions and the greater the dissolution of the metal in the bath.
- The greater the current density, the better the current efficiency. Therefore, the current density is maintained at a very high value.
- The lower the density of the bath, the higher the rate of separation of the metal liberated from the bath. The density can be lowered by using a high AlF3/NaF ratio; a ratio of slightly less than 3 is considered optimum. When the quantity of AlF3 is higher than NaF; the conductivity of the bath is decreased, the solubility of alumina is reduced, and a large volume of fluorine is produced. On the other hand, a high NaF content reduces the current efficiency due to an increase in the concentration of sodium ions and the deposition of sodium on the cathode. The sodium deposition directly lowers the current efficiency.

Refining of Aluminium (the last step)

After hall heroult process aluminium is 99.5% pure. But for some purposes, we need the metal in a more pure form, so an electrolytic process called three layered processes is used. The graphite electrode is used as cathode and carbon bottom acts a anode. Electrolytic refining takes place in a cell in which the anode is at the bottom, the current traveling through the bath and being collected at the top by graphite electrodes. A dense electrolyte forms the middle layer(a multi metal alloy).The temperature of electrolysis is about 950°C.Magnesite refractory acts as insulating wall.

At anode : Al ==>Al3 +3e-

At cathode : Al3+ -3e==> Al

Impure aluminium is dissolved at the anode to form Al3+ ions; then aluminium ions (i.e. Al3+) are deposited at the cathode in the pure form.Commercial aluminium is poured in a molten condition into the well connected with the anode alloy metal in the bottom of the cell. Current from this layer causes pure aluminium to pass through the electrolyte and float on the top layer from where it is periodically taken out. The impurities which are retained in the bottom alloy layer gradually build up and having a relatively low solubility crystallize out in the later stage. These impurities consist mainly of iron, silicon, zinc and copper entangled 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 applicable for the refining of aluminium scrap without magnesium. This process will be ineffective if the impure metal contains magnesium which may have come from Al–Mg scrap; due to magnesium reacting with the electrolyte.

Uses of Aluminum :

Due to its ideal metallic properties and cheap rates aluminium is, after copper, the most used non-ferous metal. Following are the industries where aluminium is most commonly used:

- Transportation : it is used in transportation because of its unbeatable strength to weight ratio. Its lighter weight means that less force is required to move the vehicle, leading to greater fuel efficiency.Aluminum is also known as the 'winged metal' because it is ideal for aircraft; again, due to being light, strong and flexible.Even spacecraft, such as space shuttles, contain 50% to 90% of aluminum alloys in their parts.
- Construction: Buildings made with aluminum are virtually maintenance free due to aluminum's resistance to corrosion.The lighter weight of aluminum makes it easier, faster because a building made with steel would be more heavy and would need a deeper foundation.Notable modern buildings made from aluminum include the Bank of China headquarters in Hong Kong and Zaha Hadid's London Aquatics Centre in London and Empire State Building in New York.
- Electrical: Although it has just 63% of the electrical conductivity as compaired to copper, aluminum's low density makes it the best option to be used in long distance power lines. If copper was used as wire ,supporting structures would be heavier, more huge, and more expensive. Aluminum is also more ductile than copper, making it able to be formed into wires much more easily.
- Consumer Goods: Smartphones, tablets, laptops, and flat screen TVs are being made with an increasing amount of aluminum.Apple uses predominantly aluminum parts in its iPhones and MacBooks.the normal foil used in kitchen is aluminum, as well as pots and frying pans which are commonly made from aluminum. Aluminum cans are used to package food and beverages. Coca-Cola and Pepsi have been using aluminum cans since 1967.

Recycling of Aluminum :

Aluminium recycling is the process by which scrap aluminium can be reused in products after its initial production. Recycling scrap aluminium takes only 5% of the energy used to make new aluminium from the ore. Because it involves simple remelting of scrap.For this reason, approximately 36% of all aluminium produced in the United States comes from old recycled scrap. Soda cans being the biggest part of scrap. Brazil recycles 98.2% of its aluminium can production, equivalent to 14.7 billion beverage cans per year,ranking first in the world, more than Japan's 82.5% recovery rate. Brazil has topped the aluminium can recycling charts for eight years in a row.

(*Statics source: http://recycling.world-aluminium.org/regional-reports/brazil.html)*

The effects of white dross, a waste of aluminium recycling

White dross, a residue from primary aluminium production and secondary recycling operations, usually classified as waste, still contains useful quantities of aluminium which can be extracted industrially.The process produces aluminium billets, together with a highly complex waste material. This waste is difficult to manage. It reacts with water to release a mixture of gases (including, hydrogen, acetylene, and ammonia) which ignites on contact with air; contact with damp air results in the release of ammonia gas. Despite these difficulties, the waste has found a use as a filler in asphalt and concrete.

(*Source : http://www.ohiolandfills.org/faq/aluminum-dross-saltcake/)*

Aluminum global market and demand :

Global primary aluminium production increased by 5.8 % in 2017. Continuing strong demand is also being reflected in price trends and has had an enormous impact on the level of international aluminium stocks. Aluminium will continue to benefit from the trend towards lightweight construction in coming years.In total, approx. 63.2 million tonnes of aluminium were produced worldwide in 2017.Market observers are expecting continued solid growth in the current year, (with Düsseldorf-based IKB Bank forecasting that) global primary aluminium production of 64 million tonnes and recycled aluminium production of approx. 12 million tonnes in 2018.The Aluminum Market was valued at $147.2 billion in 2018, and is expected to reach $189.8 billion by 2026.

Due to increased uses and standard metallic qualities the global aluminum demands and getting higher and higher, and the industry is expected to grow as large as iron and copper.

(*Source 1- https://www.aluminium-messe.com/en/ALUMINIUM-2020/Demand-for-aluminium-is-growing-worldwide/758/*

Source 2-https://www.alliedmarketresearch.com/aluminium-market/amp)

Health effects of Aluminum :

The reference values for the internal aluminum load (<15 µg/L in urine, <5 µg/L in serum) are very likely to be exceeded in people with occupational exposure. The biological tolerance value for occupational exposure is 50 µg of aluminum per gram of creatinine present in the urine. For aluminum welders and workers in the aluminum industry, decrease in performance in neuropsychological tests (attention, learning, memory) has been found only with aluminum concentrations exceeding 100 μg/g creatinine in the urine; manifest encephalopathy with dementia was not found. High aluminum content has been found in the brains of persons with Alzheimer's disease. It remains unclear whether this is a cause or an effect of the disease. There is conflicting evidence on carcinogenicity.

The acute toxicity of aluminum is low . No acute effects due to dietary exposure to aluminum have been observed in the general population. The toxic effects of aluminium commonly depend upon the genetic makeup and the exposure of the person. In general the metal is basically health friendly.