

Electrowinning of Aluminum

1. Aluminum

Introduction

Although it is the most abundant metallic element on the Earth's surface, the "discovery" of aluminum is of a fairly recent date. Oersted probably isolated the first metallic aluminum (impure) in 1824 –by reducing aluminum chloride with potassium amalgam–, but generally Wöhler is credited with the discovery of the metal by virtue of the first isolation of less pure aluminum in 1827 and the first description of several of its properties.

The present industrial method of production was discovered simultaneously and independently in 1886 by Paul-Louis Héroult in France and Charles Hall of Oberlin, Ohio. Their method is the basis for the world aluminum industry today. Aluminum oxide, dissolved in a sodium fluoride-aluminum fluoride fusion, is electrolyzed with direct current. Carbon dioxide is discharged on the carbon anode and aluminum is deposited on the cathode at the bottom of the cell.

Currently, in terms of scale of production (around $2\text{-}3 \times 10^7$ ton/yr worldwide) aluminum electrolysis is second in importance only to the chlor-alkali industry. This is because aluminum is both light and strong and therefore suitable for many engineering and construction applications, may readily and cheaply be treated by anodizing (cf. supra) to retard corrosion, and is the principal alternative to copper as a conductor of electricity.

Raw Materials

Aluminum, the third most abundant chemical element in Earth's crust, is usually combined with silicon and oxygen in rock-forming silicate minerals. When aluminum silicate minerals are subjected to tropical weathering, aluminum hydroxide minerals may be formed. Rock that contains high concentrations of aluminum hydroxide minerals is called **bauxite**. It is the raw material for almost all production of alumina

In 1821 the French chemist Berthier investigated a ferruginous aluminous rock (27.6% Fe_2O_3 , 52.0% Al_2O_3 , 20.4% H_2O) found near the village of Les Baux in southern France. He concluded from chemical analysis that alumina occurred as a dihydrate mineral ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) a conjecture since refuted. In 1844, the French scientist, Dufrenoy, described the Les Baux mineral as bauxite. The term bauxite now is applied generally to rocks that contain significant quantities of aluminum hydroxide minerals.

Bauxite became the primary ore for aluminum production after *Hall and Héroult* discovered an economical process for extracting aluminum from pure **alumina** (Al_2O_3) in 1886. In 1887, *Bayer* developed a process for preparing pure alumina from bauxite.

Origin of Bauxite

Bauxite exists in a great many varieties depending on its composition and occurrence in the field. The physical characteristics may range from earthy, dark-brown ferruginous material to cream or light-pink-colored layers of hard crystalline gibbsitic

bauxite. Under favorable hydrological conditions, bauxite can originate from almost any alumina-containing rocks.

It is generally believed that most bauxites were formed by tropical weathering or laterization, a leaching process by which easily soluble compounds are carried away by circulating groundwaters in alternating dry and wet seasons. Conditions which favor and intensify laterization are permeability, high temperatures, pH between 4 and 10, heavy vegetation, bacteriological action, a mature topography permitting accumulation of weathered products, and free movement of the water table with a minimum of erosion. Major world bauxite deposits consist of gibbsite from the tertiary or more recent periods. In older bauxites such as the Mesozoic deposits in Mediterranean Europe, gibbsite is dehydrated and altered to boehmite which is further altered to diaspore in the oldest-known deposits up to the Paleozoic era.

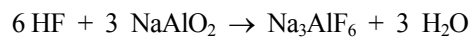
World Distribution and Reserves of Bauxite

Geological exploration during the past few decades has led to the discovery of new large deposits in *Australia, Guinea, Brazil* and *Indonesia*. World bauxite reserves were estimated in 1995 to exceed ca. 20 billion tons. The USA only has relatively small reserves (ca. 40 million tons), which is less than e.g. France (ca. 60 million tons). High-grade bauxite deposits in the United States are mainly gibbsite, found in Arkansas. Other small deposits are found in the coastal plain of Alabama and Georgia. Low-grade ferruginous bauxites occur in Oregon, Washington, and Hawaii where they have been formed from basalts. Hence the vivid interest in developing new technologies to extract aluminum from other potential resources such as clay minerals.

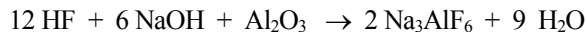
Cryolite

Cryolite is the major constituent of the Hall-Héroult cell electrolyte. High purity, natural cryolite is found in Greenland, but its rarity and cost have caused the aluminum industry to substitute synthetic cryolite.

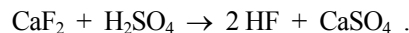
The latter is generally produced by the reaction of hydrofluoric acid with sodium aluminate from the Bayer process (cf. infra) :



or by the reaction of hydrofluoric acid and sodium hydroxide on aluminum oxide (alumina) :

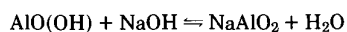
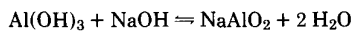


Gaseous hydrofluoric acid for the above reaction and for making aluminum fluoride is generally made by the reaction of acid-grade fluor spar with sulfuric acid :



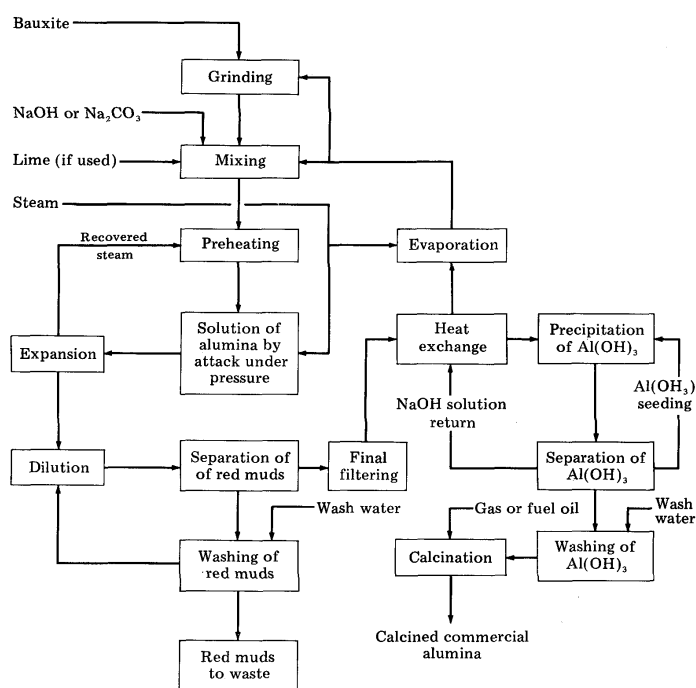
2. Manufacture of Pure Alumina

World production of alumina in 1995 totaled ca. 40 million tons. Practically all of it was obtained by processing bauxite. The first commercial bauxite extraction was that of Sainte-Claire Deville in France in 1865 but this method gave way to that of the Austrian chemist Bayer in 1887. The Bayer process, which continues to be the most economical method, takes advantage of the reaction of aluminum trihydroxide and aluminum oxide hydroxide with aqueous caustic soda to form sodium aluminate:



The reaction equilibria move to the right with increases in caustic soda concentration and temperature. The following operations are performed in turn: (1) dissolution of the alumina at a high temperature, (2) separation and washing of the insoluble impurities of bauxite (red muds) to recover the soluble alumina and caustic soda, (3) partial hydrolysis of sodium aluminate at a lower temperature to precipitate aluminum trihydroxide, (4) regeneration of the solutions for recycle to step (1) by evaporation of the water introduced by the washings, and (5) transformation of the trihydroxide to anhydrous alumina by calcination at 1450 K.

Figure 17.1 shows the flow sheet of the Bayer process. The various operations are described below.



• Figure 17.1. Flowsheet of the Bayer process.

Dissolution of Alumina by Digestion with Caustic Soda

Gibbsite, Al(OH)_3 (hydrargillite; alumina trihydrate), is the dominant mineral species in bauxites from the United States, the Caribbean, Central and South America, Africa, and Australia. This type of bauxite is the most economical to process due to gibbsite's high solubility in Bayer process liquor at a moderate temperature and pressure. Liquor containing 120-135 g/L Na_2O is used at about 140°C. Boehmite (AlOOH) and diasporite (AlOOH) are the principal minerals in monohydrate bauxites. These alumina monohydrate minerals have the same chemical composition but diasporite is more dense and harder than boehmite. Boehmitic bauxite requires temperatures from 200 to 250°C and pressures of 3.45 MPa (34 atm) or higher to obtain complete extraction of the alumina. Complete extraction from diasporic bauxite requires stronger caustic solutions, 200-300 g/L Na_2O , in addition to the higher temperatures and pressures. Whereas some bauxites may be composed entirely of one mineral phase, other

bauxites may contain all three aluminum hydroxide phases. The phase most difficult to extract sets the extraction conditions.

Associated minerals commonly found in bauxite are magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite ($\text{FeO}(\text{OH})$), siderite (FeCO_3), kaolinite ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$), ilmenite (FeTiO_3), anatase, rutile, and brookite (TiO_2).

Digestions are performed in steel autoclaves or in tubular reactors. Heat exchangers recover much of the heat content of liquor leaving the reactor to heat liquor entering it.

The digest slurry is held at temperature for an additional 15-30 min to decrease the silica concentration of the liquor by formation of an insoluble *sodium aluminum silicate*.

Separation, Washing, and Disposition of the Residues

The insoluble residues remaining after digestion are commonly known as red mud. They include iron oxides, sodium aluminum silicate, titanium oxide, and various other metal oxide impurities.

The muds may have a very fine particle size (sometimes less than 1 micron). Consequently, they are difficult to separate and wash. These operations usually are performed by continuous countercurrent decantation, the dilute wash liquors being combined with the more concentrated pregnant liquors.

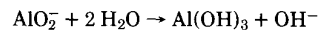
Disposal of the washed muds is a major problem. The red mud is generally disposed of by lagooning. Approximately one square kilometer of lagoon area is required for a plant processing 3.3 Mt of bauxite per year.

The same lagoon can be used for many years. Much research has been directed toward extracting the iron, titanium, chromium, vanadium, and aluminum values from the residue, but no economic processes have been developed. Unsuccessful attempts have been made to convert the mud into building products and cements. Unfortunately, the residual alkali content of the mud makes it difficult to return these lagoon areas to agricultural production.

Precipitation of Aluminum Trihydroxide

After a final filtration to remove the last traces of insoluble mud, the liquors have a $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ molar ratio between 1.5 and 1.8.

The filtered liquors are cooled to between 47 and 62°C preparatory to precipitation of about 50% of their alumina content. Precipitation requires hydrolysis of the sodium aluminate or, more correctly, of the ions AlO_2^- or $\text{Al}(\text{OH})_4^-$, to yield aluminum trihydroxide (hydrargillite), the stable solid phase in this temperature range.



To carry out precipitation on an industrial scale, aluminate liquor is seeded with the fines elutriated from previously precipitated crystals (up to four times the amount in solution) and the mixture is agitated. The seed grows to crystal agglomerates that are easy to separate and wash. Precipitation is slow, requiring 20-80 h retention in large steel agitating tanks.

Evaporation

The circulating aluminate solution, diluted by the water used to wash the muds prior to precipitation is reconcentrated to its initial concentration in large multiple-stage evaporation equipment.

Calcination

The aluminum trihydroxide from precipitation is filtered and washed, usually in rotary filters. These filters feed large rotary kilns or fluid-bed calciners where the alumina is heated to 1100-1200°C. During heating, the trihydroxide undergoes a series of changes in composition and crystalline structure with essentially no change in particle shape. The product is a white powder consisting of aggregates whose size ranges from 20 to about 200 μm .

3. Electrolysis of Alumina

General

Since the discovery of the process by Hall and Héroult, nearly all aluminum has been produced by electrolysis of alumina (Al_2O_3) dissolved in a molten cryolite (Na_3AlF_6)-based bath.

The aluminum is deposited molten onto a carbon cathode, which also serves as the melt container. Simultaneously, oxygen is deposited on and consumes the cell's carbon anode(s).

Pure cryolite melts at 1012°C but alumina and additives, namely 5-7% calcium fluoride, 5-7% aluminum fluoride, and 0-7% lithium fluoride, lower the melting point, allowing operation at 940-980°C. The system Na_3AlF_6 - Al_2O_3 has a **eutectic** at 10.5 wt % Al_2O_3 at 960°C (see phase diagram in Figure 17.2)

Joule heating from the flow of electric current is more than adequate to maintain the melt temperature.

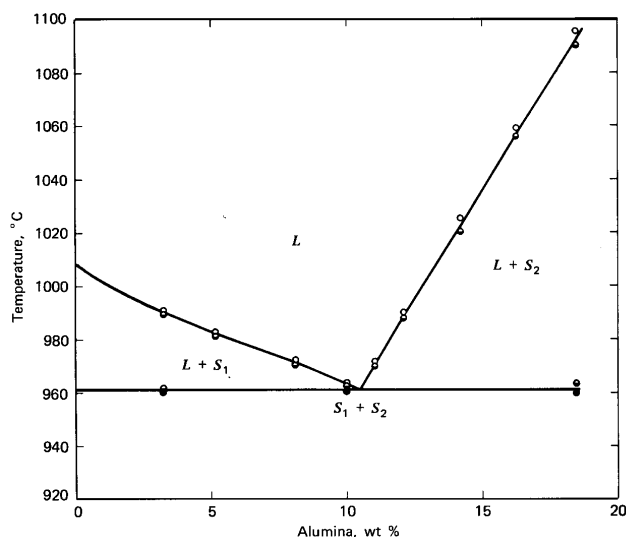
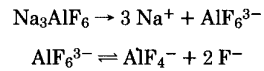


Figure 17.2.

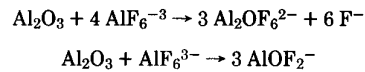
Cryolite-alumina phase diagram from 0 to 18.5% alumina. *L*, liquid; *S*₁, cryolite; *S*₂, corundum; ○, liquid; ●, liquid and solid; ●, solid.

Chemistry

Although the mechanism of electrolysis is still imperfectly understood, most investigators agree that cryolite ionizes to form hexafluoroaluminate (AlF_6^{3-}), which dissociates to form tetrafluoroaluminate (AlF_4^-), sodium (Na^+), and fluoride (F^-) ions:

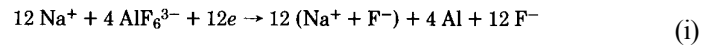


Alumina dissolves at low concentrations by forming oxyfluoride ions with a 2:1 ratio of aluminum to oxygen ($\text{Al}_2\text{OF}_{2n}^{4-2n}$); at higher alumina concentrations, oxyfluoride ions with a 1:1 ratio of aluminum to oxygen (AlOF_n^{1-n}) are formed

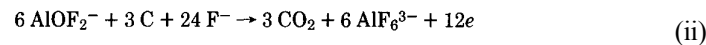


Cells are generally operated with 2-6 wt % Al_2O_3 in the electrolyte. Saturation ranges between 7-12% Al_2O_3 depending upon composition and temperature.

Ion transport measurements indicate that Na^+ ions carry most of the current; however, aluminum is deposited. Most probably a charge transfer occurs at the cathode interface and hexafluoroaluminate ions are discharged, forming aluminum and F^- ions to neutralize the charge of the current carrying Na^+ ions.



Oxyfluoride ions discharge on the anode, forming carbon dioxide and AlF_6^{3-} ions.



The addition of anode and cathode equations (i) and (ii), plus solution of alumina (eq. iii) gives the overall reaction



Current Efficiency

According to Faraday's law, one Faraday (26.80 Ah) theoretically should deposit one gram equivalent (8.994 g) of aluminum. In practice only 85-95% of this amount is obtained.

Loss of Faraday efficiency is caused mainly by reduced species (Al, Na, or AlF) dissolving or dispersing in the electrolyte (bath) at the cathode and being transported toward the anode where they are reoxidized by carbon dioxide forming carbon monoxide and metal oxide, which dissolves in the electrolyte.

Certain bath additives, particularly aluminum fluoride, lower the content of reduced species in the electrolyte and thereby improve current efficiency.

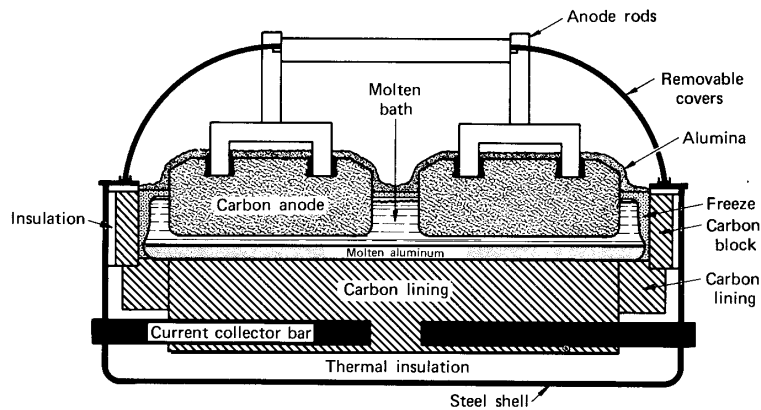
Equipment

A modern alumina smelting cell consists of a rectangular steel shell typically 9-12 m long, 3-4 m wide, and 1-1.2 m high. It is lined with refractory insulation that surrounds an inner lining of baked carbon.

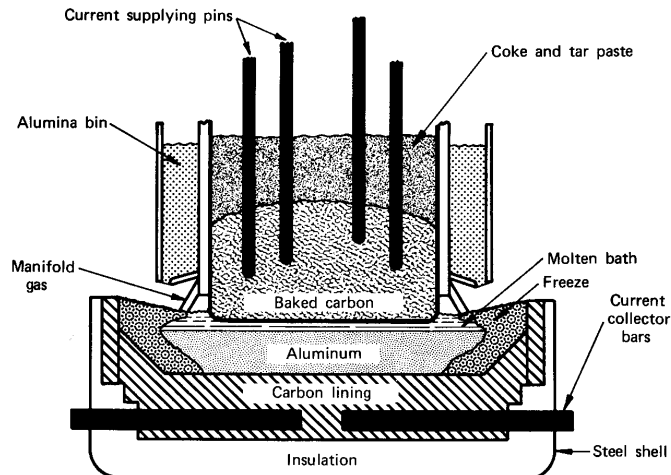
Few materials other than carbon are able to withstand the combined corrosive action of molten fluorides and molten aluminum.

Thermal insulation is adjusted to provide sufficient heat loss to freeze a protective coating of electrolyte on the inner walls but not on the bottom, which must remain substantially bare for electrical contact to the molten aluminum cathode. Steel (collector) bars are joined to the carbon cathode at the bottom to conduct electric current from the cell.

Current enters the cell either through prebaked carbon anodes (Figure 17.4) or through a continuous selfbaking so-called Söderberg anode (Figure 17.5).



• Figure 17.4. Aluminum electrolyzing cell with prebaked anode.



• Figure 17.5. Aluminum electrolyzing cell with Söderberg anode.

Prebaked anodes are produced by molding petroleum coke and coal tar pitch binder into blocks typically 70 cm wide, 125 cm long, and 50 cm high, and baking to 1000-

1200°C. Petroleum coke is used because of its low impurity (ash) content. The more noble impurities, such as iron and silicon, deposit in the aluminum while less noble impurities, such as calcium and magnesium, accumulate in the bath. Coal-based coke could be used but extensive and expensive prepurification would be required. Steel stubs seated in the anode with cast iron support the anodes in the electrolyte and conduct electric current into the anodes (Fig. 17.4). Electrical resistivity of prebaked anodes ranges from 5-6 Ω .cm. Anode current density ranges from 0.65 to 1.3 A/cm².

A Söderberg anode is formed continuously from a paste of petroleum coke and coal tar pitch added to the top of a rectangular steel casing typically 6-8 m long by 2 m wide and 1 m high (Fig. 17.5). While passing through the casing, the paste bakes forming carbon to replace the anode being consumed. The baked portion extends past the casing and into the molten electrolyte. Electric current enters the anode through vertical or sloping steel spikes (sometimes called pins). Periodically, the lowest spikes are reset to a higher level. Resistivity of Söderberg anodes is about 30% higher than prebaked anodes. Current density is lower, ranging from 0.65 to 0.9 A/cm².

End Product

Molten aluminum is removed from the cells by siphoning, generally daily, into a crucible. Normally the metal is 99.6-99.9% pure. The principal impurities are Fe, Si, Ti, V, and Mn, largely from the anode, but also from the impurities in the alumina.