

Aluminum smelting

1. HISTORY

A. Chemical displacement

Hans Christian Oersted first heated potassium amalgam with aluminum chloride and produced tiny pieces of aluminum in 1825. This was twenty years after Sir Humphrey Davy first named the metal "aluminum." Davy was the first to use electrolysis to produce samples of potassium, sodium, strontium, calcium, barium, magnesium and boron. He tried unsuccessfully for many years to produce aluminum by electrolysis. Even though he could not isolate it he was convinced that it existed and named it anyway. (Later, in much of the world, the name was changed to "aluminium" to be consistent with other metals. In North America the original spelling is still used.)

Twenty years later Wohler passed aluminum chloride vapor over molten potassium and managed to produce larger globules of aluminum. Each globule weighed only between 10 and 15 milligrams.

It was not until 1854 that a French schoolteacher, Henri Sainte-Claire Deville, substituted cheaper sodium as the reductant. He managed to prepare a small bar of aluminum. It was so precious that it was displayed next to the Crown Jewels at the Paris Exposition the next year.

The French Emperor, Napoleon III, financed Deville's work on aluminum. He hoped that aluminum could be used to make lightweight armor. Napoleon used aluminum cutlery on special occasions and had an aluminum rattle made for his young son.

The displacement of aluminum from its chloride by a more active metal worked adequately. It was of course expensive because the sodium or potassium had to be produced by electrolysis. Aluminum chloride also had to be made from naturally occurring aluminum compounds and it is a difficult compound to handle. It is volatile and tends to absorb water, which interferes with the production of aluminum.

Despite the problems, Deville was soon manufacturing two tons of aluminum each year. Over the next 20 years, technical improvements increased production to ten tons per year.

B. Electrolysis

Then, in the 1880s, a young American student, Charles Martin Hall, became interested in aluminum. He decided to develop a commercial process for extracting aluminum using an electric current. In his first experiments he electrolyzed solutions of aluminum salts in water. All he managed to produce were the gases hydrogen and oxygen.

He tried electrolyzing molten aluminum oxide. It did not work. The oxide's high melting point prevented its electrolysis. Hall tried many other substances without success.

He needed something that would dissolve aluminum oxide producing a solution that could conduct an electric current, but which would not itself be decomposed.

He began a systematic search of different salts for this purpose. In February 1886 Hall passed a direct current through a solution of alumina dissolved in cryolite (Na_3AlF_6) in a carbon crucible. After several

hours he allowed the contents to solidify. When he broke up the solid he found several small buttons of aluminum.

Within a few weeks Paul Heroult in France had independently produced aluminum by an almost identical process. Both Hall and Heroult were only 22 years old. Two years later Karl Bayer developed his process for the extraction of pure aluminum oxide from bauxite.

In 1888 Hall set up a company to manufacture aluminum. That company later became known as the Aluminum Company of America or, Alcoa.

The new process made aluminum production so much easier and cheaper that by 1891 the last Deville chemical reduction plant had closed. From only a few tons annually, five years earlier, production reached well over 300 tons in 1891.

Although Hall and Heroult are credited with the development of the electrolytic extraction of aluminum, they were not the first to have the idea. Davy, Deville and Bunsen (of burner fame) all attempted to extract aluminum using electrolysis. Deville even experimented with electrolysis of cryolite and alumina, but his only source of electric current was batteries. At that time electrolysis was too expensive for commercial production. It was Thomas Edison's invention of the dynamo and its development that made electrical power available to Hall and Heroult.

C. Other Methods

Given the high energy and other costs associated with the Hall-Heroult process, over the years the industry has looked at alternative methods of extracting aluminum. Research has explored carbothermal processes, which require temperatures greater than 2000°C for direct reduction to take place, and alternatively a process involving electrolysis of anhydrous aluminum chloride.

While such processes have been shown to produce aluminum, for a variety of technical reasons they have not been translated into viable commercial scale plants.

At the same time considerable effort has been made to improve the efficiency of the Hall-Heroult process. Before the Second World War the consumption of electricity in aluminum smelting averaged around 23.3 kilowatt hours per kilo of metal produced, whereas today, the most efficient pots run at close to 13 kilowatt hours per kilo.

These improvements owe in part to the computerization of smelting cells, an improvement that has largely been unrecognized outside the industry.

The computer takes into account the various current operating variables so that the voltage in the pot is always the best for prevailing conditions.

Other energy saving advances include -

- Improvements in bath chemistry to lower both the smelting temperature and heat losses and to increase the efficiency of the use of electrical current
- Improved insulation to reduce heat losses
- Improved baking technology for carbon anodes
- Reduced carbon anode consumption per kilogram of aluminum produced

2. THE HALL-HEROULT SMELTING PROCESS

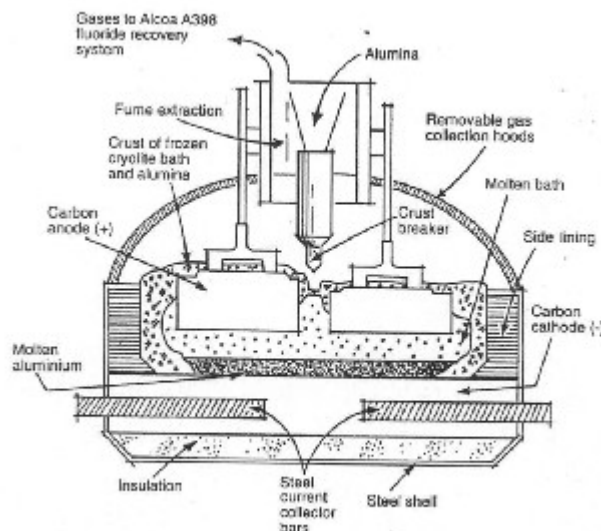
A. The Process at Work

Simply, the Hall-Heroult process is the method by which alumina is separated into its component parts of aluminum metal and oxygen gas by electrolytic reduction. It is a continuous process with alumina being dissolved in cryolite bath material (sodium aluminum fluoride) in electrolytic cells called pots and with oxidation of the carbon anodes. The bath is kept in its molten state by the resistance to the passage of a large electric current. Pot temperatures are typically around 920° - 980°C. The aluminum is separated by electrolysis and regularly removed for subsequent casting. The pots are connected electrically in series to form a 'potline.' Alcoa's Point Henry Smelter (Australia) has three such potlines at full capacity producing over 180,000 tons of aluminum per annum while the Portland Smelter (Australia) can produce some 300,000 tons annually from 2 potlines.

In each pot, direct current passes from carbon anodes, through the cryolite bath containing alumina in solution, to the carbon cathode cell lining and then to the anodes of the next pot and so on (*see Figure 1*). Steel bars embedded in the cathode carry the current out of the pot while the pots themselves are connected through an aluminum bus-bar system. The pot consists of a steel shell in which the carbon cathode lining is housed. This lining holds the molten cryolite and alumina in solution and the molten aluminum created in the process. An electrically insulated superstructure mounted above the shell stores alumina automatically delivered via a sealed system and holds the carbon anodes, suspending them in the pot.

The electrolyte, which fills the space between the anodes in the pot, consists of molten cryolite containing dissolved alumina. A solid crust forms at the surface of the electrolyte. The crust is broken periodically and alumina is stirred into the electrolyte to maintain the alumina concentration.

Figure 1. Cross section of an aluminum producing pot containing pre-baked carbon anodes



As the electrolytic reaction proceeds, aluminum, which is slightly denser than the pot bath material, is continuously deposited in a metal pool on the bottom of the pot while oxygen reacts with the carbon material of the anodes to form oxides of carbon. As the anodes are consumed during the process, they

must be continuously lowered to maintain a constant distance between the anode and the surface of the metal, which electrically is part of the cathode. The anodes are replaced on a regular schedule.

The vigorous evolution of carbon dioxide at the anode helps mix the added alumina into the electrolyte but carries off with it any other volatile materials and even some fine solids. If any carbon monoxide does form it usually burns to carbon dioxide when it contacts air at the surface of the crust. Compounds of fluoride formed in side reactions are the other main volatile product. Approximately 13 -16 kilowatt-hours of direct current electrical energy, one half kilo of carbon, and two kilos of aluminum oxide are consumed per kilo of aluminum produced.

As electrolysis progresses, the aluminum oxide content of the bath is decreased and is intermittently replenished by feed additions from the pot's alumina storage to maintain the dissolved oxide content at about 2 to 5 percent. If the alumina concentration falls to about 1.5 to 2 percent, the phenomenon of "anode effect" may occur. During anode effect, the bath fails to wet the carbon anode, and a gas film forms under and about the anode. This film causes a high electrical resistance and the normal pot voltage, about 4 to 5 volts, increases 10 to 15 times the normal level. Correction is obtained by computer controlled or manual procedures resulting in increased alumina content of the bath.

Reducing the prevalence of anode effects produces process benefits and also reduces the potential emissions of perfluorocarbons (CF_4 and C_2F_6) that are greenhouse gases.

B. Electrolyte

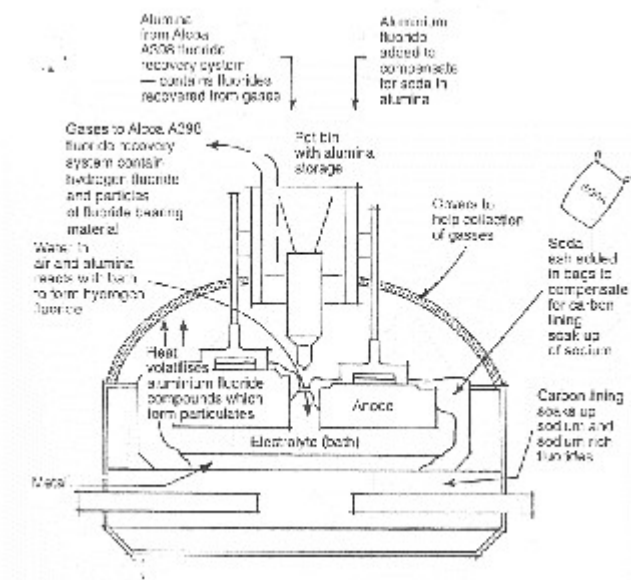
The molten electrolyte bath consists principally of cryolite (sodium aluminum fluoride) plus some excess aluminum fluoride, 6 to 10 percent by weight of fluorspar and 2 to 5 percent aluminum oxide.

The control of bath composition is an important operation in the aluminum production process. To reduce the melting point of bath (pure cryolite melts at $1009^{\circ}C$), the bath contains fluorspar and some excess aluminum fluoride, which along with the dissolved alumina, reduces the melting temperature sufficiently to permit the pots to be operated in the 920° to $980^{\circ}C$ range. The reduced operating temperature improves pot efficiency. The weight ratio of sodium fluoride/ aluminum fluoride in cryolite is 1.50; the excess aluminum fluoride in the electrolyte is adjusted to yield a sodium fluoride/aluminum fluoride ratio in the 1.00 to 1.40 range by weight.

In the first few weeks after a newly lined pot is placed in operation, the electrolyte is rapidly absorbed into the lining and insulation with a marked preferential absorption of a high-sodium- containing portion, tending to reduce the sodium fluoride/aluminum fluoride ratio below that desired. Compensation for this is made by adding soda ash (see *Figure 2*).

After the first few weeks of operation the electrolyte tends to become depleted of aluminum fluoride through volatilization of aluminum fluoride rich compounds, through reaction with residual caustic soda in the alumina, and, through hydrolysis from moisture in the air or added materials to give hydrogen fluoride.

Figure 2. Diagram of fluoride flow in pot



The volatilized fluorides and gaseous hydrogen fluoride are collected with other gases evolved from the pots by gas-collecting hoods or manifolds and are passed through large ducts to central gas treatment and recovery facilities, (see *Fluoride Recovery*).

Aluminum fluoride has to be added to the bath to match the soda content of the consumed alumina in order to maintain the sodium fluoride/aluminum fluoride ratio. The small percentage of calcium oxide as a normally occurring impurity in the alumina is sufficient to maintain the desired concentration for calcium fluoride (fluorspar).

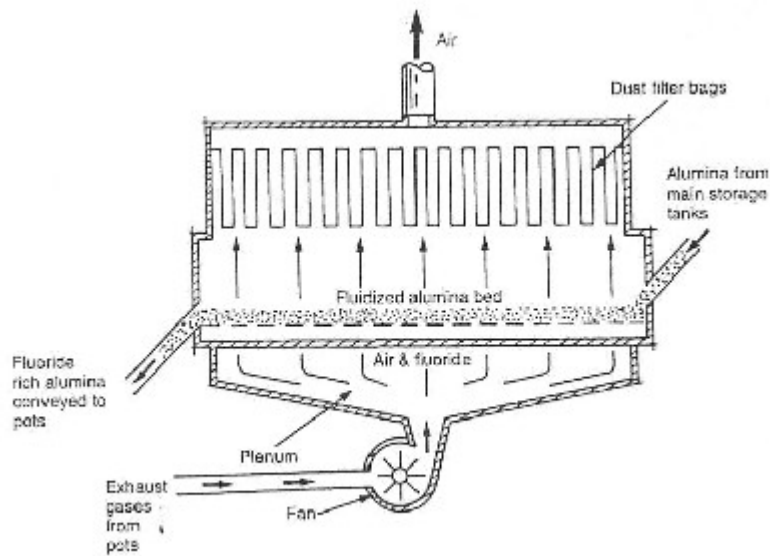
C. Fluoride Recovery

Gases and solids evolved from the pot and its electrolyte are controlled by various treatment processes. The most efficient of the commercially used methods is the Alcoa A398 Process that utilizes a highly effective pot hooding system and removes more than 99 percent of the fluoride emission from the captured pot gases. (see *Figure 3*). The A398 Process prevents air pollution, conserves valuable resources for recycling and, because it is a dry process, there are no liquid wastes to be disposed of.

Fluoride gases are passed through a bed of alumina where fluoride is adsorbed. The particulate matter is then collected in a fabric filter baghouse. The reacted or fluoride-containing alumina is recycled into the aluminum production process.

Relatively small amounts of fluoride are able to escape from the smelting process, typically during operations such as anode changing when sections of pot hooding are removed. These emissions are subject to E. P. A. discharge licenses. Continual efforts are made to improve work practices and processes to keep these emissions to a minimum.

At Alcoa operated plants, a regular check on the efficiency of emission control equipment is made by plant technical staff using a range of laboratory based and portable equipment.



E. Calculation of production and energy efficiency of a Hall-Heroult cell

Production Efficiency

For a smelting cell of 100 percent efficiency just maintained at the reaction temperature a theoretical production number can be calculated.

Avogadro's Number	= 6.0221×10^{23}
Elementary charge	= 1.6022×10^{-19} Coulombs

These numbers give the accepted value for a "Faraday" of:

One Faraday	= 96485 Coulombs
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Atomic weight of aluminum	= 26.9815
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Valence of aluminum	= 3
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One-gram equivalent weight contains Avogadro's number of atoms.

It takes 3 electrons to liberate one atom of aluminum.

Therefore every Faraday liberates 26.9815/3 grams of aluminum.

Therefore, if "I" is the current through a smelting cell, and all of this current produces aluminum, then in 24 hours every such cell makes:

$$(I \times 24 \times 60 \times 60 / 96485) \times (26.9815 / 3) / 1000 \text{ kilograms of aluminum}$$

Say the current is 180,000 amperes (typical of many smelters); then the theoretical production per cell as predicted by Faraday's Law is 1450 kilograms/day.

However, owing to electrical shorting and other electrolytic reactions and a certain amount of reoxidation of aluminum, this theoretical production is not realized. In practice the term "current efficiency" is used, this being the percentage of the current that actually results in aluminum produced.

In practice, current efficiency is generally in the order of 90 -95% so that:

Actual production per cell = Theoretical Production x CE/100.

Therefore, for example, the actual production in a 180,000 ampere cell at 90% current efficiency over 24 hours would be $1450 \times 90/100$ kilograms; i.e. 1305 kilograms.

A simplified equation for daily cell production is, therefore

Production per cell per day = (Current x CE/100 x 0.008054) kilograms

Energy Efficiency

If energy consumption is to be taken into account, then knowledge of the operating voltage of the cell is required. An estimate of this for some cells would be 4.5 volts.

The above production would therefore occur with a (DC) energy consumption of $180000 \times 4.5 \times 24/1000$ kilowatt-hours.

The electrical energy consumption per unit mass under the preceding scenario would be

$$\begin{aligned} & \text{(Current x Volts x 24/1000)} / \text{(Daily Production)} \\ & = \text{(Current x Volts x 24/1000)} / \text{(Current x CE/100 x 0.008054)} \\ \text{So, kWh/kg} & = \text{Volts/CE x 298 kilowatt-hours/kilogram} \end{aligned}$$

With the numbers given, the energy efficiency is 14.9 kWh/kg, although the most efficient plants would achieve numbers between 13 and 14 kWh/kg.

Most modern plants consist of one to six potlines, each potline consisting of 100 to 300 individual cells connected in series.

3. CATHODES AND ANODES

A. Cathodes

The carbon lining which forms the pot cavity consists of carbon blocks, preformed by external manufacturers. These blocks are placed in the steel pot shell and cemented together with a paste similar to that used in making the blocks. Thermal insulation consisting of firebrick, vermiculite, or similar materials is placed between the cavity lining and the steel shell. Large steel bars, serving as electrical current collectors, are embedded in the bottom portion of the cavity lining and extend through openings in the shell to connect with the electrical bus which links one pot to the next.

Carbon pot linings normally last from 4 to 6 years. When failure of a lining occurs, usually via the penetration of aluminum metal through to the cathode collectors, the collectors dissolve. Then, the metal and sometimes the fused cryolite bath leak around the collectors. A sudden increase in iron levels in the aluminum usually indicates that a pot is nearing the end of its service life. The lining must then be repaired at the point(s) of failure by a procedure called "patching", or else the entire lining, insulation, and

collector assembly is replaced. The latter procedure is called "relining". Pot patching and pot relining are a significant part of the production expense.

B. Anodes - Prebaked v Söderberg

Carbon anodes are a major requirement for the Hall-Heroult process. About 0.5 tons of carbon is used to produce every ton of aluminum. There are two main types of carbon anode used. Both types are made from the same basic materials and react in the same way.

A mixture of petroleum coke and pitch is strongly heated causing the pitch to bind the coke particles together. "Pre-baked" anodes are made before they are added to the pot, but "Söderberg" anodes are actually formed and baked in the pot.

The Söderberg anode uses the waste heat of reaction in each pot to pyrolyze the coke and pitch. As the lower part of the anode is consumed in the reaction, more raw materials are added at the top. During the baking process many volatile products are driven off as the pitch hydrocarbons are dehydrogenated. Solid carbon is left as the anode.

Although the Söderberg anode may be more energy efficient it is easier to treat the volatile wastes if they are not mixed with the other emissions from the pot. Dehydrogenation is often less complete in the Söderberg anode causing more hydrogen fluoride to be formed during the anode reaction. So, for environmental reasons, modern smelters use prebaked anodes.

C. Prebaked Anodes

Prebaked anodes consist of solid carbon blocks with an electrically conductive rod (e.g. copper) inserted and bonded in position usually with molten iron.

The carbon block consists of high purity calcined petroleum coke and the crushed remnants of used anode blocks bound together with pitch. The petroleum coke usually used is a by-product of petroleum refining. Its purity is important as the carbon is actually consumed in the electrolytic reaction. Any impurities present in the finished anode can pass into the metal in the smelting cell. Separating the crushed spent anode material by size allows different sized particles to be mixed so that the greatest density of packing is achieved. The component materials are mixed together in heated containers to enable the melted pitch to blend completely with the coke particles. The resulting "green" mixture is weighed accurately and formed into the required anode shape.

The green anodes are delivered to in-ground baking furnaces, which consist of a series of refractory brick lined pits with hollow, surrounding interconnected flue walls.

Anodes are packed into the pits with a blanket of coke covering the anodes and filling the space between the anode blocks and the walls of the pits. The coke often used is termed fluid coke and consists of small spherical coke particles the size of fine sand. Appropriately sized petroleum coke can also be used.

The pits are heated with natural gas for a period of several days. The flue system of the furnace is arranged so that hot gas from the pits being fired is drawn through the next few sections of pits to preheat the next batch of anodes before they are fired. Air for combustion of the gas travels through the flues of previously fired sections, cooling these anodes while reheating the air. The anodes are fired to approximately 1150°C, and the cycle of placing green anodes, preheating, firing, cooling, and removal is approximately two weeks.

The so called "ring" type furnace uses flues under draft, and since the flue walls are of dry type construction, volatile materials released from the anodes during the baking cycle are drawn into the flues. Once in the flues they burn, providing additional heat.

The baked anodes are removed from the furnace pits by means of an overhead crane on which pneumatic systems for loading and removing the pit packing coke may also be mounted.

Because the crushed, recycled anode component of a new anode has taken up fluorides during its life in the pot environment, this gives rise to a potential emission of fluorides to air during the baking process. Scrubbing equipment traps these additional fluorides for return to the smelting process.

Cleaned baked anode blocks are transferred from the bake plant storage area by conveyors to the rodding area to be made into rodded anode assemblies.

4. CASTING

Pure, molten aluminum from smelters may be cast into ingots for sale as unalloyed product or placed into melting or holding furnaces for alloying and subsequent casting into a variety of products for remelting by customers.

Some plants also cast very large ingots for rolling into aluminum coiled sheet products