

THE PRODUCTION OF ALUMINIUM

Aluminium is a light, conductive, corrosion resistant metal with a strong affinity for oxygen. This combination of properties have made it a widely used material, with applications in the aerospace, architectural construction and marine industries, as well as many domestic uses. It is only over the last century, however, that it has been possible to economically refine aluminium, due to the enormous amount of energy needed to electrolyse its oxide.

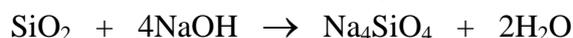
Aluminium occurs naturally as the mineral bauxite (primarily a mixture of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, Fe_2O_3 and SiO_2), and is purified in the following process.

Step 1 - Purification of raw materials

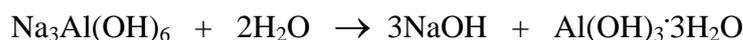
Bauxite is mined at Weipa, in Queensland, then crushed and washed to remove water soluble impurities. The remaining material is dissolved in NaOH and heated, where Al_2O_3 is selectively dissolved by the reaction



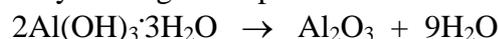
Some crystalline forms of SiO_2 can also dissolve by the reaction



These two new species are soluble, but Fe_2O_3 is a basic oxide and hence it is insoluble in this solution and can be filtered out. Over time the $\text{Na}_3\text{Al}(\text{OH})_6$ decomposes to $\text{Al}(\text{OH})_3$ (an insoluble species), which is also filtered out.

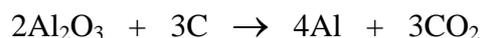
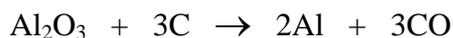


This is then decomposed by heating to temperatures above 1000°C to give alumina, Al_2O_3 .



Step 2 - Reduction of the alumina

The resultant alumina (Al_2O_3) is dissolved in molten cryolite (Na_3AlF_6), forming an ionic and electrically conductive solution. This is decomposed by electrolysis, using a consumable carbon anode with two concurrent reactions proceeding according to the following equations:



The aluminium produced is subsequently alloyed depending on the required end-product. Alloying reagents include Cu, Mg and Si and these are added in a metal treatment furnace because of the importance of precise composition control in order to impart the desired properties.

INTRODUCTION

The first aluminium to be produced commercially in New Zealand was at the New Zealand Aluminium Smelters Ltd. plant at Tiwai Point, Southland, in April 1971. The N.Z.A.S. plant is 79% owned by Comalco New Zealand Ltd. and 21% by Sumitomo Chemicals Ltd. It extracts aluminium from alumina imported from the Queensland Alumina Ltd. (Q.A.L.) refinery in Gladstone, Queensland. This is the largest alumina refinery in the world, processing the extensive ore-body in the Weipa region. Electrical energy from Lake Manapouri, Fiordland, New Zealand, is also used. Each year over 300 000 tonnes of metal

are produced and the value of the exported metal accounts for about one sixth of the annual value of manufactured goods exported from New Zealand.

Aluminium is found in many rock minerals, usually combined with silicon and oxygen in compounds called aluminosilicates. Under certain types of tropical soil weathering these aluminosilicate compounds are separated into layers of hydrated iron oxide, hydrated alumina and silica. When such deposits are rich in alumina, they comprise the mineral bauxite. The Weipa deposits are 45-55% alumina as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, with the remainder being water, iron oxide, silica and titania (TiO_2).

This plant produces about 4 million tonnes of pure alumina per year, which is shipped to smelters around the world.

Properties

Aluminium is a lightweight, durable metal. It is silvery in appearance when freshly cut, is a good conductor of heat and electricity and is easily shaped by moulding and extruding. Aluminium has two main advantages when compared with other metals. Firstly, it has a low density, about one third that of iron and copper. Secondly, although it reacts rapidly with the oxygen in air, it forms a thin tough and impervious oxide layer which resists further oxidation. This removes the need for surface protection coatings such as those required with other metals, in particular with iron.

There are five principal characteristic properties of aluminium. Comparative figures for Al, Cu and Fe are given for the first three in **Table 1**.

Table 1 - Comparisons of some of the characteristic properties of aluminium

Property	Property/Units	Al	Cu	Fe
Lightness	Density/ g cm^{-3}	2.70	8.96	7.87
Electrical conductivity	International annealed copper standard	49.6	103.6*	17.8
Thermal conductivity	$\text{J cm}^{-1}\text{s}^{-1}\text{K}^{-1}\dagger$	2.47	3.94	0.84

* w/w aluminium is a better conductor of electricity than copper.

† i.e. the heat conducted per second through a 1 cm cube of metal when the temperature difference between two faces is 1°C

In addition, aluminium has a high corrosion resistance because of the tough oxide film always present on the surface of aluminium in the presence of air, water vapour, etc., and it has a strong affinity for oxygen.

Usage

These properties lead to a variety of specialised uses.

Lightness. Use in aerospace and transport industries, as its lightness enables a greater volume of metal to be used, thus giving greater rigidity. Also used in pistons, connecting rods, etc. to give better balance, reduced friction and lower bearing loads, meaning that less energy is required to overcome inertia.

Electrical conductivity. Used extensively for electrical conductors, especially in overhead cables. However this requires a high purity grade (in excess of 99.93%).

Thermal conductivity. Extensive usage in heat exchangers, cooking utensils, pistons, etc.

Corrosion resistance. This is made use of in chemical plant, food industry packaging, building and marine applications. Aluminium paint is widely used. The oxide film can be thickened by anodising, and the film can be dyed in a wide range of colours. This is done by making the article the anode of a direct current electrolysis cell using an electrolyte solution of approximately 15% sulfuric acid.



Affinity for oxygen. This allows it to be used in explosives, as a deoxidant in steels, in thermic reactions for welding and for the manufacture of hardener alloys such as ferro-titanium. In these applications a finely powdered form (and hence a high surface area to weight ratio) is used. This property also makes possible the thermite reaction, which produces molten iron.

The thermite reaction is used by the N.Z. Railways to weld sections of rail together on the track. A mould is clamped around the ends of the two pieces of rail to be joined and any gaps sealed with sand. A previously prepared mixture of iron oxide and powdered aluminium is placed in a crucible and ignited. Ignition powders such as a mixture of barium peroxide and aluminium powder can be used, but ignition tape is more convenient. The heat from the ignition mixture starts the thermite reaction.

ignition reaction: $2\text{Al} + 3\text{BaO}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{BaO} + \text{heat}$

thermite reaction: $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} + \text{heat}$

The heat of this reaction is such that temperatures of up to 3000°C are reached and the iron formed is molten. The iron is run from the crucible into the gap between the rails which has been heated just previously with an oxy-acetylene torch. As the join cools, the mould is broken away and the excess metal trimmed off with a cold chisel and sledge hammer. The final smoothing is done with a portable grinding machine that is guided by the rail. However today nowadays direct Thermite welding is more common, powdered FeO and Al being placed between the two pieces to be jointed.

THE BAUXITE PURIFICATION PROCESS

To produce metal of high quality it is essential to start with alumina of high purity and to strictly control the reduction process. The process consists of two parts:

1. Chemical purification of raw materials to form a high purity alumina.
2. Reduction of alumina.

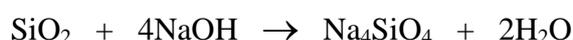
The major raw materials used in the manufacture of aluminium are shown in **Table 2**. Other raw materials include oil for manufacture of electrode blocks and the metals for alloying with pure aluminium.

Table 2 - The raw materials used in aluminium purification

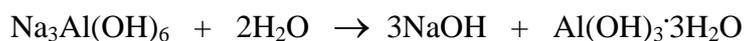
Raw material	Use	Source
Alumina (Al ₂ O ₃)	Source of Al	Gladstone, Queensland, Australia
Alaska Crude oil/heavy ends	Making coke	America
Coal	Making pitch	China, Korea
Coke, pitch	Electrode manufacture	
Cryolite (Na ₃ AlF ₆)	Dissolving alumina at 970°C	Synthetically produced
Electricity	Reduction of alumina to Al	Lake Manapouri, Fiordland, New Zealand

Step 1 - Purification of Raw Materials

At Weipa, on the northern tip of Queensland, the bauxite is open cast mined, crushed and washed before shipping around Cape York and then south down the Queensland coast to Gladstone, which is at the southern end of the Barrier Reef. There it is purified to alumina using the Bayer process which is based on the fact that silica is an acidic oxide, alumina is amphoteric and both iron oxide and titania are basic. The crushed ore is mixed with caustic soda (NaOH) solution and heated. This dissolves the alumina and some reactive crystalline forms of silica but has no effect on the iron oxide, the titania, or most of the silica which is already combined with other elements. These can then be filtered off.



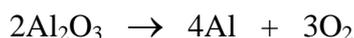
When the solution of alumina and silica is cooled, a complex aluminosilicate "sand" is first precipitated out before altering process conditions allows pure aluminium hydroxide to crystallise out. This is speeded up by initially adding a small quantity of pure crystalline aluminium hydroxide to act as sites for crystal growth.



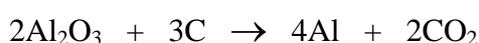
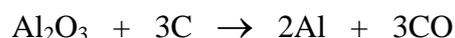
The pure crystals of aluminium hydroxide Al(OH)₃·3H₂O are heated to 1100°C, causing them to decompose to alumina (Al₂O₃) and water.

**Step 2 - Reduction of alumina**

Aluminium metal is not produced directly by the electrochemical reduction of alumina:



Rather, it is reduced by a combination of chemical and electrical energy according to the following two reactions in parallel:



This use of a consumable carbon anode lowers the required voltage by 1.0 V at the operating temperature of 950 - 980 °C.

Alumina is a covalently bonded oxide so it can only be electrolysed when the aluminium is in an ionic form. It is dissolved in molten cryolite, Na_3AlF_6 (an electrolyte, i.e. an ionic compound), and forms conducting complex anionic oxyfluorides. The electrolysis requires a large amount of energy because aluminium's affinity for oxygen makes the reaction



highly exothermic. The enthalpy of formation of Al_2O_3 is $-1676 \text{ kJ mol}^{-1}$.

The electrolysis is carried out in an electric furnace using carbon electrodes. **Figure 1** shows a cross section of a cell or electric furnace, and **Figure 2** is a photograph of one of the four pot-rooms.

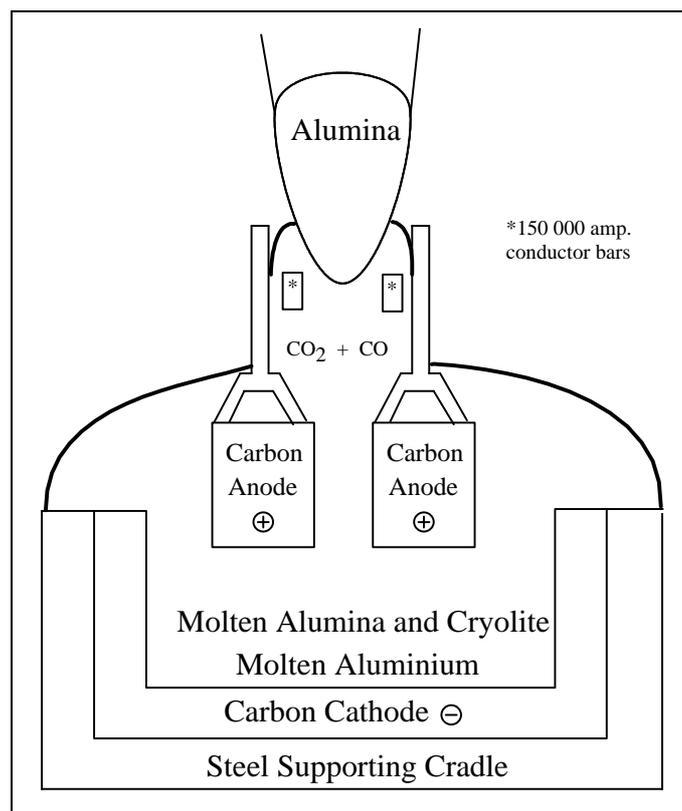


Figure 1 - Cross Section of Pot of Electrical Furnace

Each cell is four metres wide and ten metres long, and shaped like a shallow bath. The base is lined with carbon and forms the cathode on which aluminium is deposited. Suspended above the bath and dipping into the molten alumina-cryolite mix are 18 carbon blocks (the anodes) which are electrochemically oxidised using the oxide ions. Each carbon block has enough material to last 24 to 28 days in the cell.

A current of approximately 170 000 amperes is passed through each pot, with a voltage drop of 4.2 to 4.4 volts. This maintains the pot at an operating temperature of nearly $1000 \text{ }^\circ\text{C}$ as well as causing reduction of the alumina. The molten aluminium collects on the carbon cathode and is syphoned out at a rate of approximately a tonne per day.

Alloys and levels of purity

Aluminium products are produced and sold in two major groups, that of purity grades and that of alloys.

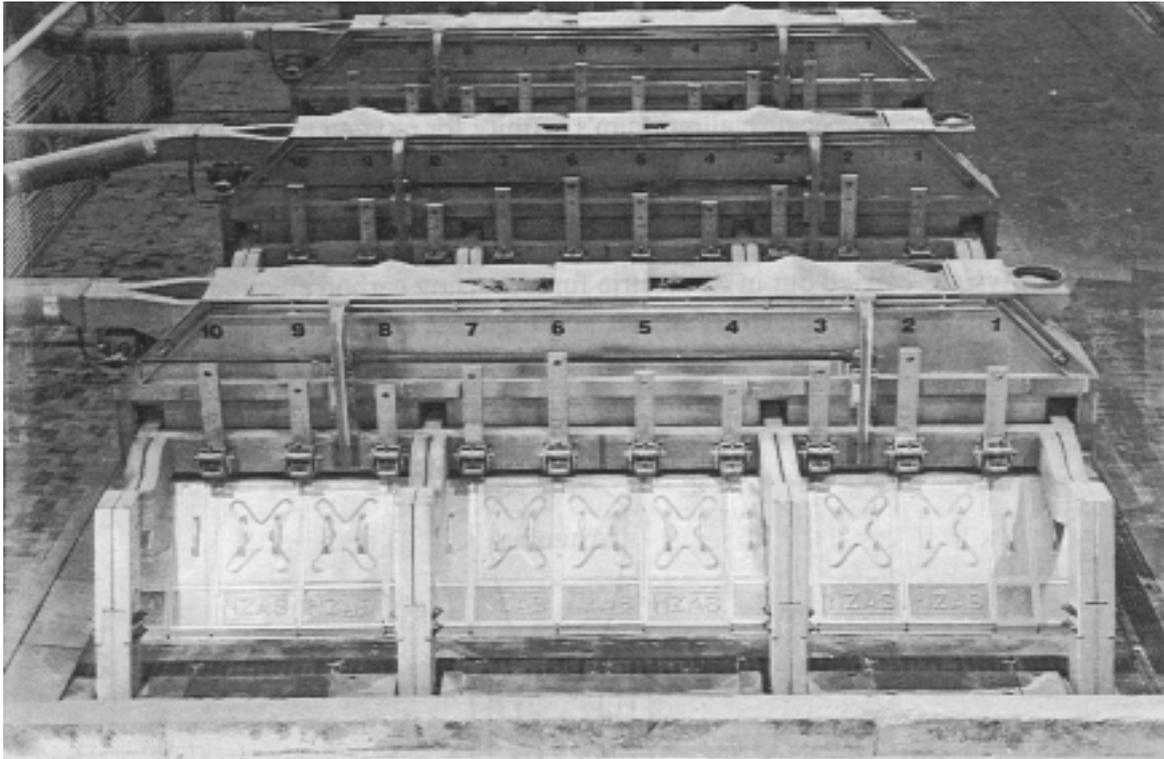


Figure 2 - One of the four pot-rooms

Purity grades

Here the aluminium content is usually the main consideration and other elements are considered only as impurities. The common grades are listed in **Table 3**.

Table 3 - Purity grades of aluminium

Aluminium content	Major impurities		Some typical uses
	Aluminium %	Iron %	
99.95 (high purity)	< 0.006	< 0.006	Extrusion joinery, electrical conductor, anodic trim, foil
99.80	< 0.15	< 0.15	Plumbing, reflectors, jewellery.
99,50	< 0.25	< 0.40	Chemical plant, tanks, tubes.
99.50	(Si + Fe) < 1.0%		Pots, pans, sheetmetal work.

Alloys

Here other elements are deliberately added to improve the properties in some way. Many alloys have been developed, the aim being to improve strength while retaining the desirable properties of aluminium, most notably its lightness and corrosion resistance. In general though, while the addition of an alloying element increases the strength, it reduces the

resistance to corrosion, making a compromise of properties necessary. A possible exception to this are magnesium alloys, which have improved corrosion resistance in marine environments. Aluminium-copper alloys have very poor resistance to corrosion, and sheets are often produced in sandwich form with thin layers of pure corrosion resistant aluminium on the outside.

A summary of typical alloys is given in **Table 4**.

Table 4 - Alloys of aluminium

Major alloy element	Content	Product	Some typical uses
Copper	Up to 4.5%	Sheet Extrusions Castings	High strength aircraft parts
Manganese	1.25%	Sheet	Sheetmetal work, pots, pans, etc.
Silicon	Up to 13%	Castings	Motor parts, castings of all types
Magnesium and Silicon	0.7% Mg 0.4% Si	Sheet Extrusions	Architectural extrusions
Magnesium	Up to 5%	Sheet	Marine uses, boats, fish boxes, beer can lids, etc.
Zinc, Magnesium and Copper	5.8% Zn 2.5% Mg 1.4% Cu	Sheet Extrusions	High strength aircraft

The strength of aluminium alloys may be further increased by:

1. Cold working operations (e.g. rolling, wire drawing)
2. Heat treatment, especially on silicon and zinc, magnesium and copper, copper and magnesium alloys, using a process called "homogenization".

Alloying is carried out by the addition of suitable quantities of the alloying element to molten aluminium. This is done in a special holding furnace, usually by adding the element direct, e.g. magnesium, iron, silicon, or a master alloy or hardener (e.g. manganese as a 10% Mn - 90% Al hardener.)

At the Tiwai Point smelter, iron and silicon are added directly to certain reduction cells, since the operating temperature is relatively high (960 °C) and this facilitates solution. Magnesium is volatile and is consequently added just before casting at about 740 °C.

At aluminium plants (e.g. rolling mills, extrusion plants), it would be normal practise to add higher melting point elements in the master alloy or hardener form. This facilitates solution of the elements at a lower temperature - many aluminium alloys are in fact true solid solutions in which atoms of alloying elements replace aluminium atoms in the crystal lattice. However it is more common for the smelter to directly supply the custom composition.

The effect of alloying, cold working operations and heat treatment are clearly shown in **Table 5**. When comparing with steels it must be noted that for equivalent sizes the aluminium alloy components will have a weight only about one-third that of the steel.

Table 5 - Tensile strengths of some aluminium alloys and steels

Purity or alloy	Typical tensile strength N/mm ² (Megapascal)
99.5%	75
99.5% cold rolled sheet	Up to 145
1½% Manganese	90
1½% Manganese cold rolled sheet	Up to 190
5% Magnesium	300
4.5% Copper	375
5.8% Zinc etc. heat treated	Up to 590
Mild steel	400
High carbon steel	950
High and ultra high tensile steels	Up to 1850

SCALE OF OPERATION

N.Z.A.S. Tiwai smelter produced about 308 000 tonnes of aluminium in 1997, and is expected to produce 325 000 tonnes per year by 1999. To supply the smelter, more than 750 000 tonnes of raw materials are shipped in by bulk loaders at the specially constructed wharf opposite Bluff Harbour.

Electricity is supplied from the National Grid, with the bulk coming from the hydroelectrical station in West Arm, Lake Manapouri, Fiordland, approximately 100 miles from the smelter. This station has a design capacity of more than 700 megawatts, about 5% of N.Z. total generating capacity.

900 people are employed at the smelter and many more are involved indirectly, either in servicing industries or in manufacturing aluminium based products.

For each tonne of aluminum produced (i.e. the daily production from each "pot" or reduction furnace), 14 000 kilowatt hours of electrical energy are used (enough to run your home for 2-3 years), together with about 400 kg of electrode carbon.

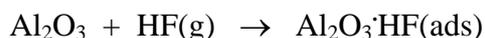
Tiwai smelter has 660 cells operating continuously, and including 48 cells using new technology developed by Comalco. The technology is the most efficient in the world operating at a Faradaic efficiency of 96.5% and using only 13 100 kilowatts per tonne.

ENVIRONMENTAL CONTROL

In the past, pollution of the environment surrounding some overseas aluminium smelters has been serious, affecting soils, vegetation, animals and humans. Substances emitted are gaseous and particulate fluorides, alumina and carbon dust, and gaseous sulfur dioxide,

carbon monoxide and carbon dioxide. Of these, the fluorides are of the most environmental concern, potentially causing damage to humans selected plant and animal life.

The fluoride fumes are emitted more or less constantly and are roughly 50% particulate (condensed cryolite droplets and condensed sodium tetrafluoroaluminate vapour) and 50% gaseous HF. More than 98% of the fluorides are removed by the 'dryscrubbing' process in which the cell emissions are passed over a moving bed of alumina. HF is removed by adsorption on the alumina surface:



Particulates are physically trapped by the alumina at the same time. The alumina used in the dry scrubber is transported to the reduction cell, and used to form aluminium, and the fluoride which was lost from the cell, returned. The scrubbing system used at NZAS was designed by Comalco and built in New Zealand, and is currently the best scrubbing system in the world.

As part of a pre-operational investigation, many hundreds of samples of plant material ranging from *Pinus radiata* to gladioli and silver beet were tested to determine background fluoride levels. Hundreds of urine samples from farm stock were also tested. These tests were carried out by D.S.I.R., University of Otago, Lincoln College, Department of Health and the Ministry of Agriculture and Fisheries. Using the results of this work, standards were set for the protection of this area.

Before the plant was commissioned, four farms were chosen as permanent grazing monitors, and a number of sheep, dairy and beef cattle subjected to regular urinary testing, biopsy sampling, dental and other veterinary inspections. A 200 acre experimental farm was established in an area where meteorological data suggested any fluoride contamination could be greatest. Infrared and colour aerial photographs were taken of the surrounding area before production and at six monthly intervals since, to provide a continuous check on vegetation patterns.

So far, air fluoride levels at Tiwai are well below predictions and meet the standard for the atmosphere outside this area, i.e. one part per billion by volume over a one month period. This is helped by the high frequency of west-north-west winds, a characteristic of the locality which influenced the siting of the smelter.

None of the livestock on the grazing monitor farms show any symptoms of dental fluorosis, loss of production, or other changes attributable to the smelter. Effects of smelter pollution on animals at the Tiwai experimental farm is far less than was predicted, being limited to mild dental fluorosis, which is confined to staining, and was relatively common locally before the setting up of the smelter.

An environmental health programme was established whereby smelter personnel exposed to fluorides are checked at regular intervals.

The perfluorocarbons (PFC's), CF_4 and C_2F_6 are also of environmental concern. PFC's are emitted intermittently, during anode effect, when the alumina concentration is too low and cryolite is reduced instead.



Although the total amount of CF_4 and C_2F_6 emitted is low compared with HF and particulate fluorides, these have very high greenhouse effect potential. CF_4 and C_2F_6 are very unreactive, and because of this there is no method available to remove them. Instead the strategy used worldwide and at NZAS, is to minimise their emission in the first place by minimising the number of anode effects.

Results of all checks carried out by N.Z.A.S. and independently by the Department of Health are freely exchanged. N.Z.A.S. has entered into an agreement to operate the Tiwai smelter within prescribed fluoride levels which are the most exacting anywhere in the world. Failure to meet these requirements means the closure of this plant.

N.Z.A.S. have produced a booklet entitled "The Bluff Aluminium Smelter".

This article for volume one of the 1st edition was written by P. Fitzgerald (Southland Boys High School) and G. French (N.Z. Aluminium Smelters Ltd.) with the thermite section contributed by E.C.G. Fletcher (Hastings Boys High School). This has been extensively revised by Barry Welch and Margaret Hyland (Chemical and Materials Department, School of Engineering, University of Auckland) after editing by Heather Wansbrough, with reference to:

Grjotheim, K. and Welch, B. J.; *Aluminium Smelter Technology - a Pure and Applied Approach*(2nd. ed.); Aluminium-Verlag; 1988