HOW IS ELECTRICITY USED TO PRODUCE ALUMINIUM AND WHAT ARE THE IMPLICATIONS FOR SOCIETY?

Introduction

This investigation focuses on the industrial production of aluminium by electrolytic reduction and the application of Faraday's Laws to estimate the energy demands and production cost. In doing so, 3 chemical concepts shall be explored: (1) Redox reactions and equations, (2) Stoichiometry and (3) Energy. This investigation also explores the economical and environmental impact of aluminium production and use.

Why Electrolysis?

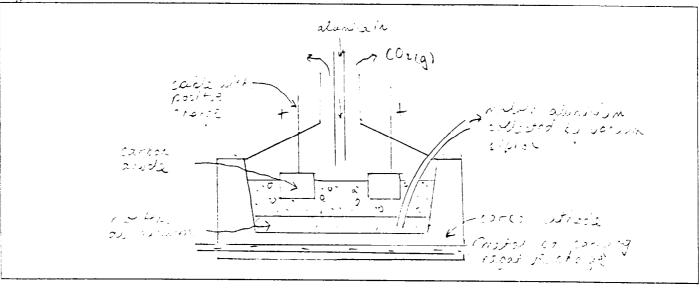
To obtain aluminium metal, Al^{3+} ions must be reduced to Al. Because Al^{3+} is a weak oxidant, it doesn't react spontaneously (i.e. without electricity) with many chemicals. The few chemicals that Al^{3+} does react spontaneously with are expensive, thus chemical reduction isn't used. The cheaper alternative is to force a reaction using electricity. This process is called electrolysis, where electrical energy is converted to chemical energy. This allows non-spontaneous reactions to occur where reactive substances (e.g. Al) are the products, rather than the reactants. Electrolytic production of aluminium is called the Hall-Heroult process. This involves reduction of alumina (Al_2O_3), which is first extracted from bauxite ore.

The Hall-Heroult Smelting Process

In the Hall-Heroult process, the aluminium and oxygen in alumina (Al₂O₃) are separated by electrolysis¹. An electric current is passed through molten alumina to initiate a series of redox reactions, thus reducing Al⁺ ions to Al(I). The process takes place in a Hall-Heroult cell, referred to as a 'pot' in the industry. Smelters consist of 100-300 pots connected in an electrical series, called a 'potline'.



Figure 1: A Hall-Heroult Cell²



The important features of a Hall-Heroult cell are: the electrolyte, anodes and cathode. An electrical power supply forces electrons from the anodes to the cathode, causing the anodes to be positively charged and the cathode negatively charged. As a result, O^{2-} anions in the electrolyte are attracted to the anode and Al^{3+} , cations are attracted to the cathode.

The Electrolyte

Alumina must be molten so that Al^{3+} and O^{2+} ions separate and become mobile. This allows Al^{3+} and O^{2+} particles to migrate to different sides of the cell, thus isolating aluminium. Pure alumina melts at $2050^{\circ}C^{3}$. However, solvents can reduce the melting temperature, thus lowering energy costs.

To determine what substance is used as the solvent, the electrochemical series can be consulted. This is a list of half-cell equations. Each equation has an E° value (measured in volts) which indicates its tendency to occur as a reduction reaction - the higher the value, the greater the tendency. On the top left are the strongest oxidants. On the bottom right are the strongest reductants.

Figure 2: The electrochemical series

	Oxidants		Reductants		<u>E°(V)</u>
↑	$Zn^{2}(aq) + 2e^{-}$	\rightarrow	Zn(s)	1	-0.76
increasing	$2H_2O(1) + 2e^{-1}$	\rightarrow	$H_2(g) + 2OH^*(aq)$	increasing	-0.83
. oxidising	$Al^{3+}(aq) + 3e^{-}$	→	Al (s)	reducing	-1 71
strength	$Mg^{2}(aq) + 2e^{-}$	\rightarrow	Mg (s)	strength	-2.38
	Na (aq) + e	\rightarrow	Na (s)	↓	-2.71
	$Ca^{2+}(aq) + 2e^{-}$	\rightarrow	Ca(s)		-2.87



Unlike in the electrowinning of most other metals, $H_2O(l)$ isn't used as solvent. For Al^{3-} ions to be reduced, it must be the better oxidant. However, according to the electrochemical series, $H_2O(l)$ is a better oxidant than Al^{3+} (refer Figure 2). Therefore, instead of Al^{3+} (aq) being reduced, the $H_2O(l)$ would participate in the reduction reaction.

To overcome this problem, cryolite (Na₃AlF₆(l)) is used instead of $H_2O(l)$. Cryolite is a poorer oxidant than Al^{3+} , so it won't compete with Al^{3+} for reduction. Hence, alumina is dissolved in cryolite solvent at 950-1000°C⁴. Alumina is added at intervals to replace that decomposed by electrolysis.

The Negative Electrode: The Cathode

The cathode is the negatively charged base of the cell. It is made of graphite, which is non-corrosive in molten cryolite and aluminium, and remains solid at 1000°C^{5} . The Al³⁺ ions in the electrolyte migrate to the cathode, attracted by the negative charge. Each ion receives 3 electrons and forms aluminium metal on the cathode. The alumina reduction equation is⁶:

$$Al_2O_3$$
(in cryolite) + 6e⁻ $\rightarrow 2Al(1) + 3O^{2-}$ (in cryolite)

Aluminium, which melts at 660°C, is therefore molten and sinks to the bottom of the cell because it is denser than molten cryolite⁷. Thus, the cathode is located at the base of the cell.

The Positive Electrodes: The Anodes

The anodes are made from reactive carbon and are immersed in the electrolyte. The O^2 ions in the electrolyte migrate to the anodes, attracted by the positive charge. The anions react with the positively charged carbon to form $CO_2(g)$. The carbon oxidation equation is⁸:

$$C(s) + 2O^{2}$$
 (in cryolite) $\rightarrow CO_{2}(g) + 4e^{-}$

As the carbon anode decomposes, more must be replaced regularly.

The overall redox equation for aluminium production is:

$$2 \text{ Al}_2\text{O}_3(\text{in cryolite}) + 3\text{C(s)} \rightarrow 4\text{Al(l)} + 3\text{CO}_2(g)$$

The alumina and carbon reactants are constantly fed into the cell and molten aluminium product is constantly removed via a vacuum siphon. Le Chatelier's Principle states "If an equilibrium system is subject to a change, the system will adjust itself to partially oppose the effect of the change". By keeping the equilibrium unbalanced, the system will continually try to restore equilibrium by a net forward reaction which produces aluminium.



For the Hall-Heroult process to be commercially viable, the following are required 10:

- cheap and abundant electricity;
- cheap and readily available cryolite and alumina;
- anodes and cathodes made of carbon (which is inexpensive);
- locations that allow inexpensive and quick transport of materials and products;
- low electrolyte temperatures to minimise heating costs and equipment wear;
- continuous operation.

Calculating Approximate Energy Demands and Production Cost

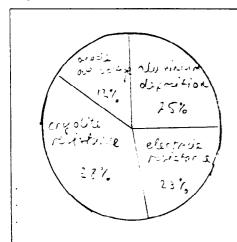
To calculate energy demands, Faraday's Laws of Electrolysis can be applied. These are:

Faraday's First Law: The mass of metal produced at the cathode is directly proportional to the quantity of electricity passed through the cell¹¹ or $m \propto Q$

<u>Faraday's Second Law</u>: In order to produce one mole of a metal, one, two, three, or another whole number of moles of electrons must be consumed¹².

The theoretical voltage required in each cell is 4.610V¹³, but about 5.000V¹⁴ is used since converting electrical energy to chemical energy isn't 100% efficient. Energy can be lost through resistance in the cables, measuring devices, activation energy and heat. Current is responsible for the speed of production - the greater the current, the faster the process - and about 150,000A¹⁵ is used. Below, the energy consumption distribution of a typical cell is depicted.

Figure 3: Energy Consumption Distribution¹⁶



Only 25% of the energy goes into the actual aluminium production reaction. Cryolite resistance consumes the most energy but it is not wasted because it helps maintain the electrolyte temperature at 950-1000°C.



Energy Demands of Producing 1 Tonne of Aluminium

First, find the amount in moles.

$$n(Al) = \frac{m(Al)}{M(Al)} = \frac{1000000}{26.98} = 3.706 \times 10^4 \text{ mol}$$

According to Faraday's Second Law, Al^{3+} (in cryolite) $+ 3e^{-} \rightarrow Al(1)$.

∴
$$n(e^{2}) = 3 \times n(Al)$$

= $3 \times 3.706 \times 10^{4} \text{ mol}$
= $1.112 \times 10^{5} \text{ mol}$

The charge (Q) on 1 mole of electrons is 1F (F = faraday), which equals 96,500 C (C = coulombs) 17 .

Since Q =
$$n(e^{-}) \times 96,000$$

$$\therefore Q = 1.112 \times 10^{5} \times 96,000$$

$$= 1.067 \times 10^{10} C$$

The charge can now be used to find energy (E) in kilojoules (kJ). Since $E = V \times I \times t$ and $Q = I \times t$,

∴ E = V × Q
=
$$5.000 \times 1.067 \times 10^{10}$$

= 5.337×10^{10} J
= 5.337×10^{7} kJ

Since 1 kJ \times 60(seconds) \times 60(minutes) = 1 kilowatt hour (kWh)

$$\therefore 1 \text{ kJ} = \frac{1}{3600} \text{ kWh}$$

$$\therefore 5.337 \times 10^7 \text{ kJ} = \frac{5.337 \times 10^7}{3600} \text{ kWh}$$

$$= 1.483 \times 10^4 \text{ kWh}$$

The amount of energy needed to produce 1 tonne of aluminium is about 14,830 kWh of electricity, which covers successful energy conversions as well as losses.

Cost of Producing Aluminium per Day

The cost of aluminium production per day depends on the amount produced. The Alcoa-owned Point Henry smelter produces 182,000 tonnes annually 18, an average of 498.630 tonnes per day.

In Victoria this year (1996), 'Powercorp' supplies electricity to the aluminium industry at 2.24 c / kWh¹⁹.

Therefore, the average cost of electricity per day for aluminium production at Point Henry



\$165,640.90 spent per day on electricity is expensive. The aluminium industry is constantly trying to find new ways of reducing its energy requirements. As a result, this has significant effects on both economic and environmental factors.

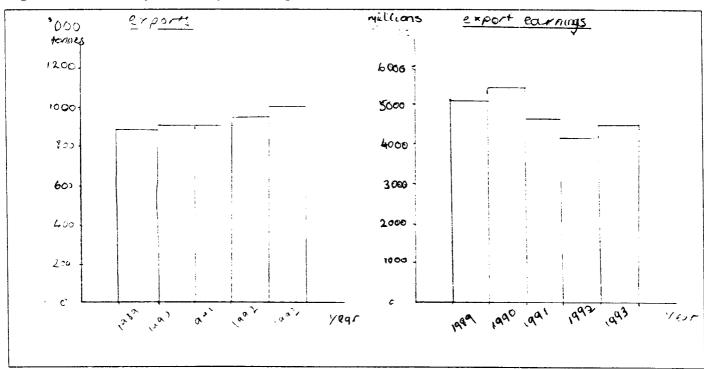
Economic and Environmental Implications

Economic Implications

Australia produces about 40% of world bauxite and over 35% of world alumina, making it the largest producer of bauxite and alumina²⁰. Australia is also one of largest producers and exporters of aluminium in the world. One advantage Australia has over its competitors is its close proximity to Asian markets, which are the fastest growing markets for aluminium²¹.

Producing aluminium adds value to bauxite ore by 100 times²². In 1993, the aluminium industry exported , 1,030,000 tonnes of aluminium ingot and 97,000 tonnes of semi-fabrications, generating \$4.4 billion to the nation's wealth²³.

Figure 4: Australia's Exports and Export Earnings²⁴



The aluminium industry provides jobs for some 69,000 Australians directly and 21,000 indirectly²⁵. The industry further benefits Australians through dividends to company shareholders and provides material for other industries, especially those shown below.

Figure 5: Domestic Use of Aluminium²⁶

INRULTRY	1. ALUMINIUM DISTRIBUTION			
	1980	1003		
building and constructing	34.75	35.02		
packaging	26.74	28.39		
electrical	13.33	9.04		
machinery and equipment	9.75	10.74		
transport	9.35	12.92		
· consumer durables	6.03	3.89		

Since electricity accounts for 20-25% of the total production cost²⁷, the aluminum industry is concerned with reducing energy requirements. Early this century, about 23,300 kWh were required to produce 1 tonne of aluminium. Today's technology allows the same amount to be produced with about 15,000 kWh - a saving of 30%²⁸. Furthermore, the recycling of used beverage cans saves up to 95% of the energy otherwise required to produce aluminium from bauxite²⁹.

Environmental Implications.

Electricity used to produce aluminium is manufactured mainly by burning coal, which is a non-renewable energy-resource. The by-products of coal burning include $CO_2(g)$ and $SO_2(g)$. $CO_2(g)$, with its great capacity to insulate heat, is now a major contributor to the 'Greenhouse Effect'³⁰ (global warming). Also, both $CO_2(g)$ and $SO_2(g)$, when in high concentrations, react with atmospheric moisture to form acid rain³¹:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(l)$$

$$SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(l) + H_2(g)$$

Acid rain pollutes lakes, rivers and forests, killing the flora and fauna that live in those habitats³². Furthermore, the used cooling-water from power stations is discharged into nearby lakes and rivers, causing 'thermal pollution' which kills aquatic life³³.

Pollution is also caused directly from aluminium smelting. Again, $CO_2(g)$ is the main by-product. It is produced at the anodes according to the oxidation equation: $C(s) + 2O^2$ -(in cryolite) $\rightarrow CO_2(g) + 4e^2$. About 1.22 tonnes of $CO_2(g)$ is produced per tonne of aluminium. This is calculated accordingly:

For 1 tonne of Al,

$$n(Al) = \frac{m(Al)}{M(Al)} = \frac{1000000}{26.98} = 3.706 \times 10^4 \text{ mol}$$

Since
$$2 \text{ Al}_2\text{O}_3(\text{in cryolite}) + 3\text{C(s)} \rightarrow 4\text{Al(1)} + 3\text{CO}_2(g)$$
,
 $\therefore \text{n(CO}_2) = \text{n(Al)} \times \sqrt[3]{4}$
 $= 3.706 \times 10^4 \times \sqrt[3]{4}$
 $= 27795 \text{ mol}$

$$m(CO_2) = n(CO_2) \times M(CO_2)$$

= 27795 × 384
= 1,222,980 g
 \approx 1.223 tonnes

The gas by-product also contains fluoride toxins, which come from cryolite reaction with atmospheric moisture³⁴.

$$2Na_3AlF_6(1) + 3H_2O(1) \rightarrow Al_2O_3(s) + 6NaF(s) + 6HF(g)$$

In high doses, fluorides can be damaging to humans and wildlife. However, modern treatment facilities such as 'dry scrubbers' now remove 99% of the fluoride content, in compliance with the Clean Air Licence as set by Environmental Protection Authorities³⁵.

Much effort has gone into environmental-protection programs by the industry. Alcoa has about 30 full-time employees, including biologists, industrial hygienists, soil scientists, and ecologists, engaged in environmental



work³⁶. On top of this, Alcoa is providing \$6.5 million to support Landcare activities such as re-vegetation, rehabilitation of degraded wetlands and education³⁷.

Health - Recent research indicates a possible link between aluminium and Alzheimer's disease which affects the nervous system³⁸. Evidence also suggests that aluminium compounds could trigger anaemia and bone diseases³⁹. As yet, these theories aren't definite, however many manufacturers of consumer goods (e.g. Kraft, Sara Lee and some deodourant manufacturers⁴⁰) have already removed aluminium-containing compounds from their products.

Conclusion

All commercial production of aluminium today relies on electricity to power the Hall-Heroult process. During this process, electricity is passed through electrolytic cells to initiate Al^{3+} reduction. This takes place at the graphite cathode of each cell. O^{2-} anions, which are also contained in the electrolyte, oxidise the carbon anodes to form $CO_2(g)$, the main by-product.

The Hall-Heroult process is the cheapest way known of extracting aluminium. To be commercially viable, electricity and materials such as cryolite and carbon must be readily and inexpensively obtainable. Also, smelters need operate continuously and be located in areas where transport of materials and products is inexpensive and quick. Because these requirements are met, electrolysis continues to dominate aluminium production.

The major problem faced by the industry today is minimising pollution, which has both an economical and environmental impact. Throughout this century, technological developments has meant that the electrical energy required to produce aluminium has dropped by 30%. However, the problem of excessive $CO_2(g)$ emissions remains. $CO_2(g)$ is a major contributor to the Greenhouse Effect and can form acid rain, which kill aquatic life and vegetation. Recent research has also indicated a possible link between aluminium and Alzheimer's disease.

Nevertheless, aluminium production is economically desirable. Each year, the industry generates billions of export dollars and provides thousands of Australians with jobs. Due to the metal's various properties, aluminium is a valuable material to many industries and thus society in general.

Information Evaluation

Regarding electrolytic smelting of aluminium, the most up-to-date information available was from information sheets and booklets issued by companies and authorities such as: Alcoa, Alcan, Comalco, the Australian Science Teachers Association and the Aluminium Development Council.

However, slight variations occurred regarding the energy demands and the total cost of production was omitted altogether. Some of the sources were subject to bias as they tended to 'sell' the industry, focusing heavily on the economic benefits. In relation to the environmental issue, the information concentrated mainly on what was being done to protect the environment rather than the actual damage caused by the industry.

(This CAT contains 1992 words)

Acknowlegements

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Endnotes

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