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A SURVEY OF POTENTIAL PROCESSES FOR THE MANUFACTURE OF ALUMINUM

Contract No. 31-109-38-4210

by

ARTHUR D. LITTLE, INC.

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FINAL REPORT ON

A SURVEY OF POTENTIAL PROCESSES FOR THE MANUFACTURE OF ALUMINUM

PREPARED FOR

THE OFFICE FOR ELECTROCHEMICAL PROJECT MANAGEMENT
ARGONNE NATIONAL LABORATORY
UNDER CONTRACT NO. 31-109-38-4210

BY

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DECEMBER 1979

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This effort was directed by the ANL Office for Electrochemical Project Management, N.P. Yao, Director, with G.M. Cook as Project Manager.

ABSTRACT

This study considers the following alternative processes to the Hall-Heroult cell for the production of primary aluminum - direct carbothermic reduction of alumina; reduction of bauxite to an aluminum-silicon alloy; the subchloride process; the disproportionation of aluminum sulphide; the production through a nitride intermediate; and electrolysis of aluminum chloride, aluminum sulphide and aluminum nitride; and plating from non aqueous solvents. Comparisons of energy consumption are made with current Hall-Heroult technology and with projected improved technology - particularly titanium diboride cathodes and permanent anodes.

The major conclusion is that the only alternative technology at present is the Alcoa chloride electrolysis process but that sulphide and nitride electrolytic processes offer potential advantages in the future. With the exception of thermal reduction to an aluminum - silicon alloy none of the carbothermic processes is competitive because they require electric furnaces. Significant improvements in energy consumption could be achieved with titanium diboride cathodes in the Hall-Heroult cell though a long lived cathode has yet to be demonstrated.

TABLE OF CONTENTS

Table of Contents (continued)

1.0 SUMMARY AND CONCLUSIONS

Primary aluminum production, exclusively by the Hall-Heroult process, consumes nearly 5% of the electrical energy generated in the United States; this corresponds to the consumption of 7-8 kWhr/lb. of aluminum produced. This report describes a study of both the Hall-Heroult process and alternative methods to define what practical opportunities exist to reduce electrical energy consumption, areas where R&D are necessary to implement these opportunities and the capital investment involved.

We have confined our attention to operations related directly to aluminum or aluminum alloy production. That is, we have not looked at alumina production by the Bayer or any alternative extraction processes. Our sources of information were the open literature (primarily patents), discussions with members of the aluminum industry in the U.S. and Canada, interaction with the group at the University of Trondheim in Norway (for European activities) and a recent committee report of the Light Metals Society and Light Metals Refining Association of Japan. Our approach was to look for opportunities for new processes based on new technology and to reassess projects and processes previously rejected or put in abeyance.

The alternative processes that we examined were:

- fourteen methods for direct carbothermic reduction of alumina to the metal;
- direct reduction of bauxite to an aluminum-silicon alloy;
- the sub-chloride process;
- sulphide disproportionation process;
- the nitride process;
- chloride electrolysis;
- sulphide electrolysis;
- nitride electrolysis;
- non-aqueous electrolysis;
- miscellaneous processes.

These processes were then compared with existing Hall-Heroult technology in terms of electrical energy consumption and total energy requirements.

The basic information that we have collected on these processes is set out in Table 1.

Our general conclusion is that with the exception of chloride electrolysis (Alcoa Smelting Process) there is no technology to produce aluminum metal that can compete in electrical energy consumption with the Hall-Heroult process. For the future there are some possible alternatives-sulphide or perhaps nitride electrolysis, or a modified sub-chloride process that replaces the prereduction step with direct treatment of the ore with aluminum chloride. Each of these concepts requires a significant amount of research before promise might be identified.

All the non-electrolytic processes require very high temperatures that can only be achieved in an electric furnace and in each case we estimate that the electrical energy consumption (typically 8-10 kWhr/lb.) is in excess of that required in a Hall-Heroult cell (6-8 kWhr/lb.)

However, an opportunity does exist for the direct reduction of bauxite to an aluminum-silicon alloy in a blast furnace type of operation. Oxygen rather than air must be used to attain the high temperatures but the overall thermal energy requirements are about one third those of the Hall-Heroult process. The presence of the silicon simplifies the high temperature chemistry and the end product is a casting alloy for which there is a large market. Research into this concept is in progress.

Production of aluminum by the electrolysis of aluminum chloride in a fused chloride melt is proven technology (Aloca Smelting Process, ASP). Alcoa has operated a 15,000 ton/yr plant though current operations are at a lower level to prove out new ancillary technology. The Electrolytic step consumes 4.5 kWhr/lb of aluminum, but the additional step compared to the Hall Heroult process - the formation of aluminum chloride from alumina - requires more thermal energy than the formation of prebaked anodes for the Hall-Heroult cell. The net effect is that the total energy consumption of the Alcoa Smelting Process is only marginally better than Hall-Heroult. Capital and operation costs of the Alcoa Smelting Process are estimated by us to be comparable to those of Hall-Heroult.

A low temperature (<200°C), chloride electrolysis process operating at quite high current density was described in the recent patent literature but it appears that the operating voltage (up to 11V/cell) is too high for it to compete in electrical energy consumption.

Other electrolytic approaches with aluminum sulphide or nitride offer the opportunity for lower electrical energy operations (<6 kWhr/lb)

PROCESS	DESCRIPTION	ELECTRICAL ENERGY CONSUMED kWh/lb	THERMAL ENERGY EQUIVALENT 10^6 BTU/ton	OTHER THERMAL ENERGY CONSUMPTION 10^6BTU/ton	TOTAL ENERGY 10^6BTU/ton	COMMENTS
Hall-Heroult (HH)	Electrolysis of Al_2O_3 in Na_3AlF_6 melt at 960°C in 50-200 KA cells with consumable carbon anode, aluminum pool cathode	6.0-8.0	125-165	25*	150-190	Long established technology, uniquely used world wide in large scale production of aluminum. High electrical energy demand may be reduced by 20-25% with TiB_2 cathodes and permanent anodes-subjects of current research which should be intensified and accelerated.
Alcoa Smelting Process (ASP)	Electrolysis of $AlCl_3$ in LiCl.NaCl melt at 700°C with multicell bipolar stack of graphite electrodes-anode not consumed	4.5	95	35	130	Advantage of lower electrical energy demand than HH, Disadvantage that high purity $AlCl_3$ needed. Economically competitive operation not yet demonstrated publicly. Proprietary process so no action recommended.
Direct Carbo-Thermic Reduction To Aluminum	Arc furnace reduction of alumina with petroleum coke.	8.0-14.0	165-290		165-290	Very high temperatures needed (~2010°C) reduction process in complicated by the formation of Al_4C_3 and Al_4O_4C, volatility of Al and AlO and back reaction of Al and CO reform Al_2O_3.
Direct Carbo-Thermic Reduction to Al-Si Alloy	Oxygen blown blast furnace type operation reducing bauxite with petroleum coke	-	-	70	70	Thermal reduction to a commercially useful alloy is very attractive. Al-Si-O-C system should be vigorously studied and practical problems of large scale operation should be actively considered.
Subchloride or Gross Process	Prereduction of bauxite in electric furnace followed by exposure to $AlCl_3$ vapor which selectively removes aluminum metal as AlCl. Subsequent cooling produces aluminum according to $AlCl \rightarrow 2Al + AlCl_3$	8.6	180	-	180	Very extensively studied by Alcan who concluded that it was more electrically energy intensive than H-H. Might be feasible if the bauxite were reduced in an oxygen blown furnace. This aspect should be examined.
	Prereduction in blast furnace	2.8	60	60	120	

*As fuel and consumable materials in anode fabrication

PROCESS	DESCRIPTION	ELECTRICAL ENERGY CONSUMED kWh/lb	THERMAL ENERGY EQUIVALENT 10^6 BTU/ton	OTHER THERMAL ENERGY CONSUMPTION 10^6 BTU/ton	TOTAL ENERGY 10^6BTU/ton	COMMENTS
Disproportionation of Aluminum Sulphide (Al_2S)	Reaction of Al_2O_3 with recycled Al_2S_3 in the presence of C gives Al_2S. Subsequent cooling produces Al according to $3Al_2S \rightarrow Al_2S_3 + 4Al$	10	210	-	210	Technically a difficult process with both low pressure and high temperature operation. Due to significant solubility, contamination of the aluminum with sulphide is very likely.
Nitride Intermediate	Formation of the nitride according to $Al_2O_3+3C+N_2 \rightarrow 2AlN+3CO$ in an induction furnace. Nitride decomposed under vacuum to give aluminum	NA			NA	Batch process, energy intensive, contamination with carbonitride is difficult to avoid.
Sulphide Electrolysis	Formation of Al_2S_3 followed by electrolysis in a fluoride or chloride fused salt bath to give aluminum and sulphur	5.0-6.0	100-125		100-125	This approach is sufficiently attractive in view of its low electrical energy requirements-to warrant experimental studies to better define the uncertainties in the chemistry. These uncertainties include the means to manufacture Al_2S_3 in high yield and the effect of soluble monovalent aluminum sulphur complexes that are formed at the cathode and oxidized at the anode on the current efficiency.
Nitride Electrolysis	Electrolysis of AlN as $Li_3N.AlN$ dissolved in cryolite at 727°C	3.6	75	60	135	Low energy process even if AlN made by reaction of $AlCl_3$ with NH_3, because of low decomposition voltage (0.79V) for AlN. Bench scale demonstration only - chemistry not understood.

PROCESS	DESCRIPTION	ELECTRICAL ENERGY CONSUMED kWh/lb	THERMAL ENERGY EQUIVALENT 10^6 BTU/ton	OTHER THERMAL ENERGY CONSUMPTION 10^6BTU/ton	TOTAL ENERGY 10^6BTU/ton	COMMENTS
Monochloride Process	Aluminum is extracted from bauxite with aluminum chloride at 1800°C	6.5	135		135	Laboratory demonstration only, on a large scale electrical energy requirement might be expected to be similar to the Gross process i.e. slightly greater than the H-H process.
Toth Process	Reduction of aluminum chloride with manganese metal. Manganese chloride is converted to the oxide then reduced to the metal in a blast furnace	10-12 (See Comments)	210-250	80	290-330	Managanese oxide cannot be effectively reduced in a blast furnace, so that the process as specified would not operate satisfactorily. There are prospects for electrolytic regeneration of the managanese at an energy requirement of 3.5-4.0 kWhr/lb Mn. (≡10.5-12.0kWhr/lb Al)

Table 1 (cont'd)

but the preparative methods for the feedstock are not easy and are quite energy intensive.

The above comments should be viewed against potential reductions in energy consumption with improved Hall-Heroult technology.

A significant improvement in energy consumption (perhaps up to as much as 20%) can be realized by using titanium diboride cathodes in the Hall-Heroult cell. However, no one has yet been successful in demonstrating a lifetime that would justify the capital investment associated with their use. A life of some two to three years is needed; the best reported to date is six to eight months. The problems are cracking and spalling and there is as yet an incomplete understanding of the factors that are important in titanium diboride manufacture and use. (The fabrication of long-lived titanium diboride structures is being pursued by outside manufacturers rather than by the aluminum industry itself.)

The development of a permanent anode is a bigger challenge and though there are some large-scale tests in progress in Europe and Japan and many laboratory studies in the U.S., there are no reports of success. It is anticipated that although the depolarizing influence of the carbon used in present-day anodes is lost, an improvement in cell voltage efficiency (perhaps up to as much as 10%) would be realized with a permanent anode because of a much-reduced anode cathode distance tnat results from dimensional stability. A carbon monoxide or hydrogen depolarized anode is considered to be beyond practicality.

More immediately, some improvement in Hall-Heroult cell efficiency (up to 5%) can be achieved with sophisticated controls. The pattern of individual cell voltage variations can be monitored and analyzed to anticipate anode effects (a large voltage increase associated with depletion of alumina in the melt) and to optimize anode positioning. Higher energy costs are also an inducement to operate cells at lower current densities which realize better efficiency.

Low temperature electrolysis in non-aqueous electrolytes can produce deposits of aluminum but the current densities are an order of magnitude below the chloride or cryolite melts. This means larger capital investment for equivalent capacity. This does not appear to be an attractive approach.

The overall perspective is that there is alternative technology to the Bayer-Hall-Heroult approach to produce aluminum but for the most part it does not compete on energetic or economic grounds. The non-electrolytic production of aluminum-silicon alloys is an exception to the above comment.

Our basic recommendations are:

- to intensify activities to produce a long lived titanium diboride cathode;
- an analysis of the technical and economic factors to determine the impact of titanium diboride cathodes on energy consumption, production levels and operating costs in the aluminum industry and from this analysis establish a strategy for retrofitting;
- to continue the search for a long-lived inert anode;
- to carry out the necessary basic studies of the Al-O-Si-C system and engineer a practical demonstration of the thermal reduction of bauxite to an aluminum-silicon alloy;
- to continue the development of a mathematical model of the dynamic characteristics of the Hall-Heroult cell with a view to achieving control in established cells.
- to pursue basic research on the kinetics of the carbothermic reduction of alumina and bauxite;
- to study the manufacture of aluminum sulphide from natural ores and the subsequent electrolysis of the sulphide;
- to examine the prospects for the electrolysis of aluminium nitride.

2.0 INTRODUCTION

Aluminum is produced by the Bayer-Hall-Heroult (BHH) process; the first step (Bayer process) is the manufacture of alumina from bauxite ores; the second is an electrolytic step (Hall-Heroult) in which the alumina, dissolved in a cryolite melt, is reduced to aluminum metal. Several exhaustive descriptions of the Bayer-Hall-Heroult process are available in the literature, they are listed in the appended bibliography.

The BHH approach, in use for more than eighty years, is, with one exception, the only process used throughout the world for producing aluminum today. The exception is a chloride electrolytic process developed by Alcoa (the Alcoa Smelting Process, ASP). Also, there are extensive studies of processes to produce alumina from domestic ores other than bauxite, but none is commercially practiced at the present time.

Significant quantities of energy go into aluminum production(1), an estimated 217 x 10^6 BTU/ton as thermal energy, of this 27 x 10^6 BTU/ton goes to the production of alumina, the balance; 190 x 10^6 BTU/ton, goes to generate electricity for the electrolytic step and to produce carbon anodes which are consumed on a stoichiometric basis during electrolysis. Total electrical energy consumption for the production of aluminum ($\sim$7 kWhr/lb) is nearly 5% of the total generated in the United States.

There is therefore a great incentive to reduce energy consumption in aluminum production and particularly to define a non-electrolytic process for the production of the metal. Even the electrolytic process offers the opportunity for significant energy savings since the current industry average of close to 7 kWhr/lb is far in excess of the theoretical requirements of just under 3kWhr/lb. The approach that we adopted in this study was to examine each of the selected aluminum production processes in terms of technical feasibility and energy consumption. We have classified the processes as direct carbothermic reduction, indirect reduction (sub-halide process, sulphide disproportionation and nitride process) and alternative electrolytic processes. More detail is given in Table 1.presented in the Summary. We have confined our attention to the energy intensive step of producing aluminum metal and have not looked at alternatives or improvements to the Bayer process.

3.0 ELECTROLYTIC PRODUCTION OF ALUMINUM BY THE HALL-HEROULT PROCESS

Since all comparisons in this report will be made with respect to Hall-Heroult technology it is perhaps advisable to set out the basic facts on this process. Extensive literature is available and is listed in the bibliography. Improvements to the basic technology are considered in a later section.

All Hall-Heroult cells are essentially the same in basic design with the exception that there are two types of anode. The cell consists of a horizontal cathode of carbon in a carbon lined, steel bath; the anodes are suspended immediately above the cathode so that the separation between them and the aluminum pool that forms on the cathode is approximately 2" or less. The electrolyte is molten cryolite, Na_3AlF_6, with a slight excess of AlF_3 at 940-975°C. It is also common practice to add lithium carbonate to the cell to improve the conductivity. The two types of anode are the prebaked and the Soderberg. As the name implies the prebaked anodes are formed from coke (derived from anthracite or petroleum) and pitch, in a separate operation. It is important that the starting materials produce little ash which otherwise ends up as impurity in the cell. The Soderberg anodes are formed continuously in-situ by the heat of the cell from a paste of petroleum coke and pitch. The terms horizontal and vertical applied to the Soderberg cell refer to the configuration of the anode current collectors and not to the attitude of the anode. Some idea of the size of the Hall-Heroult cells can be gathered from their operating currents in the range of 50 to 250 kA with anode current densities of 600-800 ASF. The cross section of a typical cell and two types of Soderberg cells are given in Figures 1, 2 and 3.

In operation, alumina, produced by the Bayer process, is dissolved in the cryolite to the extent of about 5 wt%. The alumina is preheated by pouring it onto the crust of frozen electrolyte that insulates the top of the cell. The alumina is then added by breaking the crust periodically. Overfeeding a cell leads to sludge formation which is difficult to disperse and might lead to days of down time. It is usual to control the alumina addition by depleting the cell leading to an anode effect. The anode effect is a large increase in voltage associated with the formation of a gas film at the anode. The monitoring and control of the anode effect is discussed in more detail in a later section. The principal operational variable is the anode cathode distance (ACD). In a normal cell the level of the aluminum cathode pool rises by about 1.5 to 2.0 cm/day, about the same rate as a prebaked cathode is consumed. Adjustment is, in principle, needed only when aluminum is tapped off, however, anode consumption is not uniform and although this effect is self compensating, external correction is often beneficial. The importance of the ACD will be more apparent after the discussion of energy losses below.

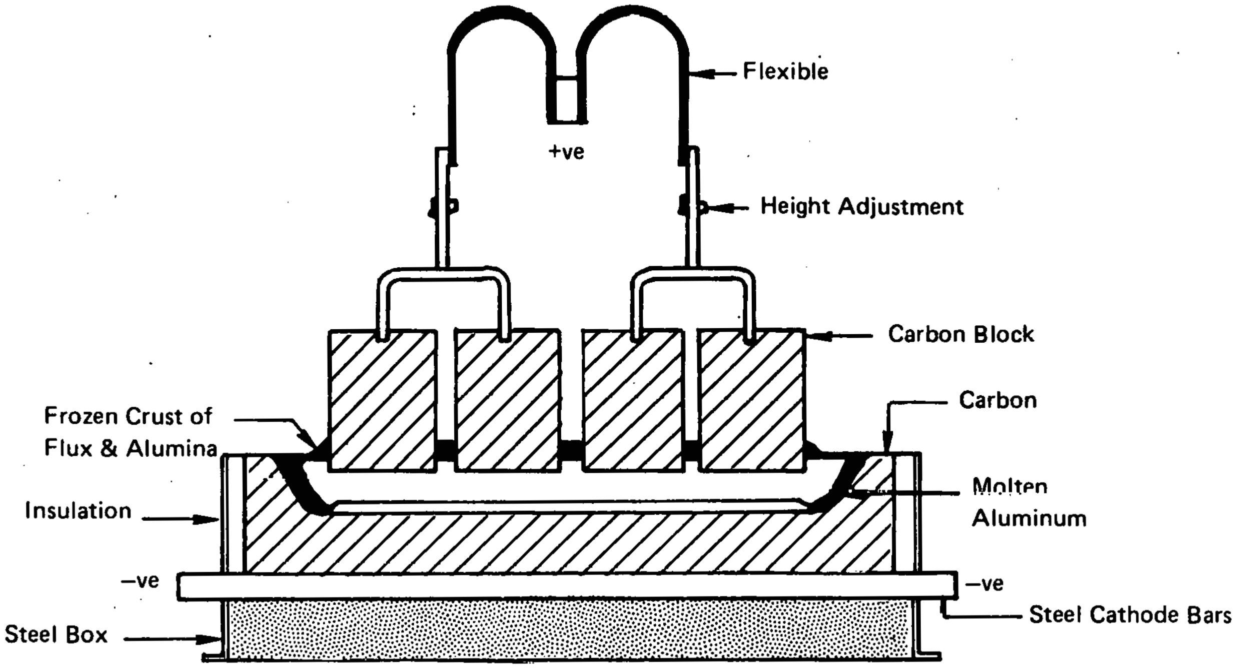


FIGURE 1 AN ELECTROLYTIC FURNACE WITH BAKED BLOCK ANODE

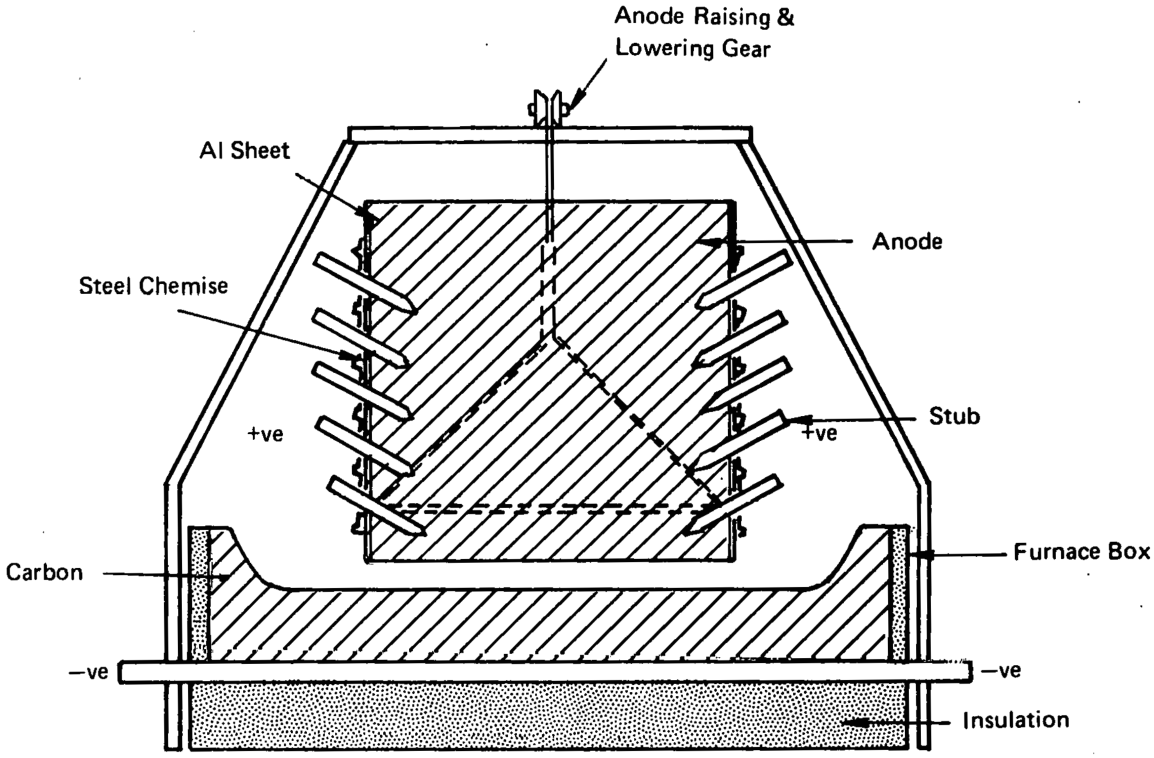


FIGURE 2 ELECTROLYTIC FURNACE WITH SIDE-STUB SODERBERG ANODE

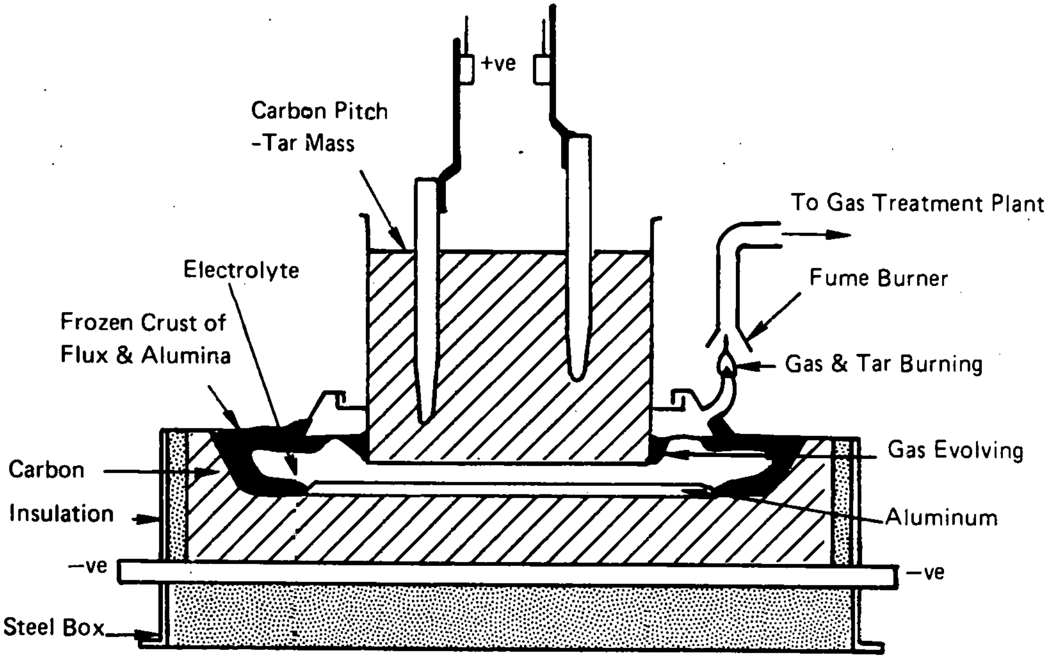


FIGURE 3 ELECTROLYTIC FURNACE WITH VERTICAL STUBS

The theoretical energy requirement for the reduction of alumina in an electrolytic cell with a consumable carbon anode according to the scheme

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

is 2.85 kWhr/lb of aluminum. This is based on a reversible voltage for this reaction of 1.17V. In practice the production of aluminum consumes from 6 to 8.5 kWhr/lb at cell voltages of 4.5V and higher. The breakdown of the voltage drop across a typical prebake cell operating at 145 kA and a 2" ACD is given in Table 2. The irreversibility of the electrochemical processes (0.5V) and the resistance of the aluminum carbide film formed at the interface of the aluminum pool with the carbon cathode (0.4V) make significant contributions. However, it is apparent that the predominant loss is due to the resistance of the electrolyte which in turn is strongly dependent on the ACD.

The ACD is typically close to 2" to prevent shorting due to surges in the aluminum pool that result from the magnetic field in and around the cell. This problem becomes more intense the bigger the cell and the higher the current density, though improved understanding of these interactions has minimized their effect in modern cells.

The other factor to be considered in energy consumption is current efficiency. A back reaction is possible between molten aluminum and the carbon dioxide generated at the anode:

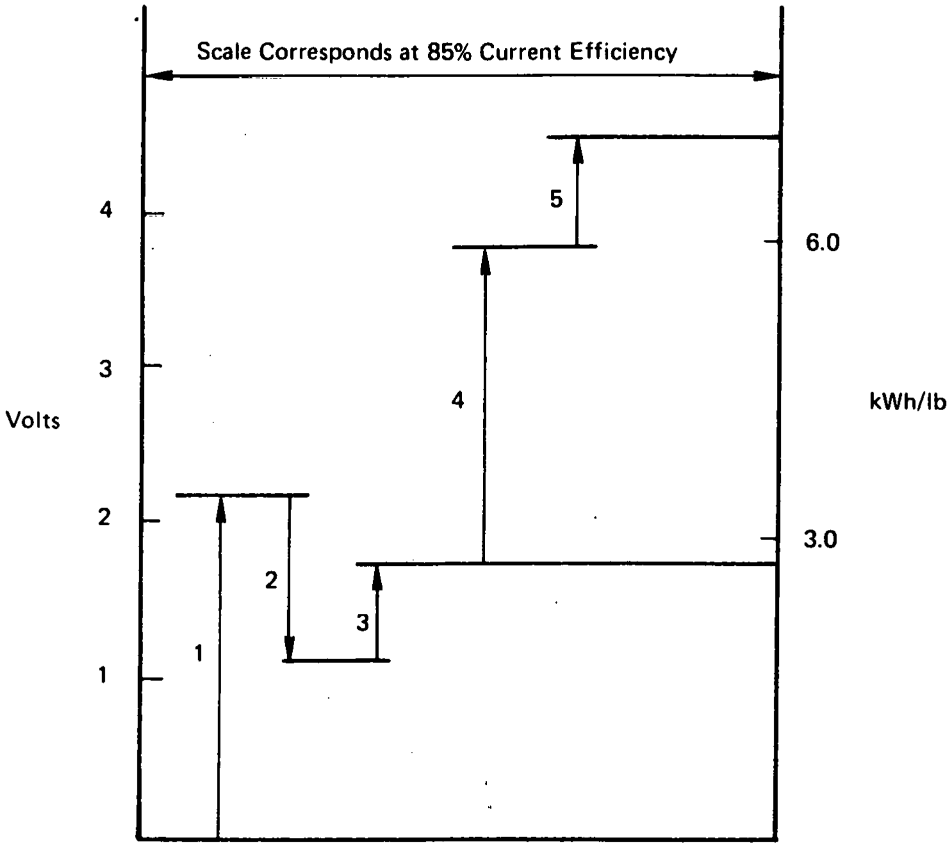
$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO$$

In all probability the mechanism for this reaction is contact between a fog of aluminum metal in the electrolyte (generaged by the electromagnetic mixing) and bubbles of carbon dioxide coming off the anode. This is obviously affected by the ACD; at a separation of 2", typical current efficiency would be in the 85-90% range.

We have recently updated our previous estimates of Hall-Heroult process production costs, these are presented in Tables 3 and 4. Based on a capital investment of $340 million for a 160,000 ton/yr plant the production cost is $800/ton or 40¢/lb.

TABLE 2

VOLTAGE LOSSES IN HALL–HEROULT–CELL



1.	Decomposition Voltage of Alumina	2.2V
2.	Depolarizing Effect of Consumable Anode	1.0V
3.	Polarization Losses	0.5V
4.	IR Loss in Bath	1.9V
5.	IR Losses in Electrodes and Current Collectors	0.8V
	Time Averaged Anode Effect (not shown)	0.1V

TABLE 3

ESTIMATED COST OF PRODUCING PRIMARY ALUMINUM NEW CONVENTIONAL HALL-HEROULT REDUCTION PLANT (1979)

Annual Capacity-160,000 Short Tons/Year
Capital Investment-338,016,000

Raw Materials	Units	$/Units	Units/Ton	$/Ton	
Alumina	tons	140	1.930	270.20	
Calcained Delayed Coke	tons	125	.205	25.63	
Fluid Coke	tons	102	.202	20.60	
Hard Pitch	tons	133	.121	16.10	
Cryolite	tons	480	.015	7.20	
Aluminum Fluoride	tons	465	.030	13.95	
					353.68
Utilities					
Power Cells	kWhr	.015	14,340	215.10	
Auxiliary	kWhr	.015	460	6.90	
Fuel	10^6xBTU	2.00	11	22.00	
					244.00
Labor					
Operating and Maint.	man hrs	12.45	6.4	79.68	
Supervision and Adm.	man hrs	17.70	2.2	38.94	
					118.62
Operating Supplies					
Cast Iron	tons	195	.004	.78	
Soda Ash	tons	230	.001	.23	
Fluorspar	tons	180	.004	.72	
					1.73
Maintenance Materials					
Cathode Blocks	tons	1100	.012	13.20	
Anthracite	tons	182	.006	1.09	
Soft Pitch	tons	200	.0006	.12	
					14.41
Maintenance, Supplies					7.60
Plant Overhead @ 50% of Labor					59.31
Total Production Costs Before Depreciation and GS&A					799.35
					40¢/lb

Source: Arthur D. Little estimates

TABLE 4

ESTIMATED CAPITAL COST BREAKDOWN OF A NEW PREBAKED ALUMINUM REDUCTION PLANT -- CAPACITY 160,000 SHORT TONS/YEAR
U.S. LOCATION

Components	Cost Current Dollars (1979)
Alumina and Carbon Storage	8,736,000
Mobile Equipment	1,344,000
Carbon Paste Plant	6,384,000
Green Carbon Plant	24,528,000
Carbon Baking Plant	31,920,000
Carbon Rodding Plant	18,480,000
Substation	4,032,000
Rectifiers	22,848,000
Potlines	45,696,000
Bus Bars	29,568,000
Structures & Ventilation	56,448,000
Metal Casting	20,832,000
Utilities excluding Power Plant	16,128,000
Support Facilities and Pollution Control	51,072,000
TOTAL	338,016,000

Source: Arthur D. Little estimates

4.0 DIRECT CARBOTHERMIC REDUCTION

4.1 Introduction

Direct reduction of aluminum in a blast furnace type of operation, avoiding the use of electrical energy, has long been the dream of aluminum manufacturers. There is not only the energy savings associated with the inefficiencies of electrical power generation, but also, potentially, a large decrease in capital costs.

The problems that have prevented realization of a practical process are the high temperatures required to reduce alumina and the complexity of the chemical reactions involved.

4.2 Chemistry of the Carbothermic Reduction of Aluminum

Carbothermic reduction has been considered in the literature (3, 4, 5, 6) and though some of the early work is confusing, the thermodynamics of the Al-O-C system are now well defined. Directly relevent publications are listed in the Bibliography. When carbon and alumina are heated there is no substantial reaction until a temperature of some 1800°C is reached, though there are claims that reduction starts as low as 1500°C (7). However, the product of the reaction is not aluminum metal but aluminum carbide,

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO.$$

This is further complicated by a secondary reaction, a loose association of the carbide with unreacted alumina to form the oxycarbide Al_4O_4C,

$$4Al_2O_3 + Al_4C_3 \rightarrow 3Al_4O_4C.$$

No free carbide is formed unless the carbon content of the melt exceeds the stoichiometry defined by the above equation or the temperature is raised to above 1950°C.

The important point is that even at this temperature no free aluminum metal is formed. The phase diagram for the Al_2O_3-Al_4C_3 system set out in Figure 4 summarizes the situation. It also demonstrates that a temperature in excess of 2100°C is necessary before aluminum is formed, probably according to the reaction.

$$Al_4O_4C + Al_4C_3 \rightarrow 8Al + 4CO.$$

At even higher temperatures the carbide will decompose though the carbon will remain dissolved in the aluminum.

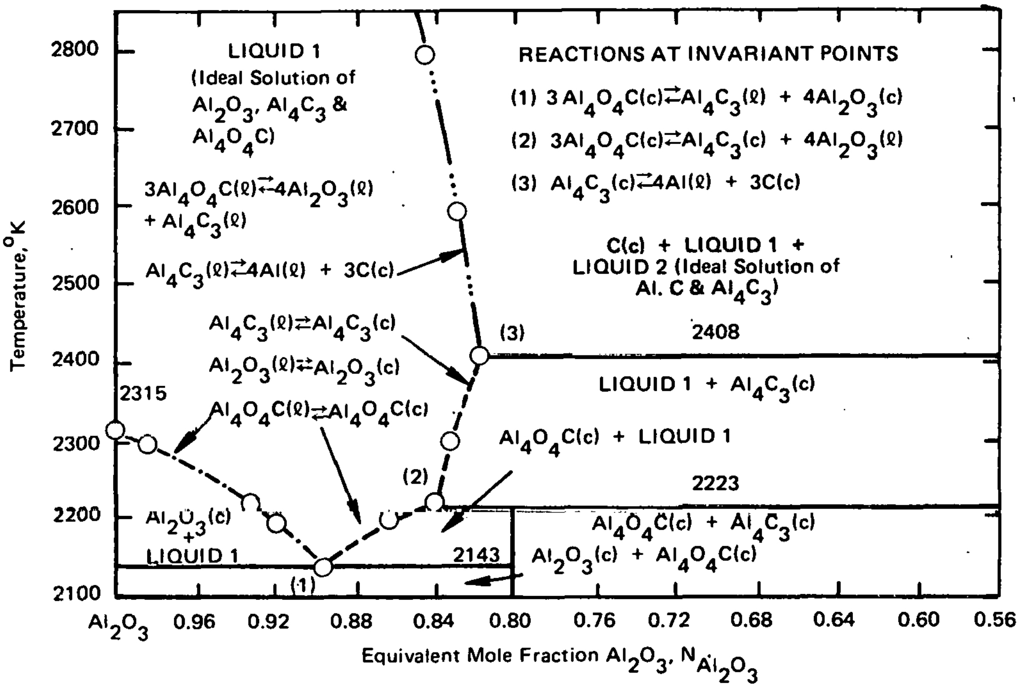


FIGURE 4 CALCULATED PHASE DIAGRAM FOR Al_2O_3–Al_4C_3 SYSTEM

Source: Cochran, U.S. Patent 3 971 653

Two further factors complicate the recovery of aluminum, one is the volatility of aluminum and of Al_2O that can be formed at the higher temperatures, the second is the back reaction of aluminum in the gas phase with carbon monoxide on cooling. Though this reaction may not be complete it results in unacceptable quantities of alumina and aluminum carbide in the product.

The practical recovery of aluminum is assisted by the fact that the oxycarbide and aluminum/aluminum carbide liquid phases are immiscible so that isolation of an aluminum-carbon phase is possible. If careful control can be exercised in the C to Al_2O_3 ratio in the feed, the carbon content of the metallic phase can be minimized. The desirability of this is apparent from the phase diagram of the Al-C system set out in Figure 5.

On the negative side, the oxycarbide melt is viscous and sticky and very difficult to handle. The practical approaches described in the literature are exclusively electric arc or plasma furnaces with sealed operation to maintain good thermal efficiency. The walls are typically lined with carbon, protected from reaction by a layer of frozen melt. Vapor losses (∿25% of the aluminum is in the gas phase under equilibrium conditions) are usually minimized by condensation on the charge. Several processes are suggested for the separation of the carbide from the metal, with the carbide being recycled.

In each of the descriptions given below a figure is quoted for the electrical energy required in the reduction process. If the information was available in the Patent or could be derived from information provided, then that figure is cited. Otherwise the figure was estimated by us using the following approach. We assumed a heat of reaction at 2100°C of 160 kcal/mole (5295 kcal/kg Al) for

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO,$$

that the back reaction reduced the conversion efficiency to 80% and that the furnace operated with 65% thermal efficiency. The energy to preheat the alumina (specific heat 0.33 cal/g) and coke (specific heat 0.50 cal/g) to 2100°C was also taken into account. As set out in Table 5 the basic electrical energy requirement is 7.6 kWhr/lb. If the product is recovered in vapor form an additional 2.3 kWhr/lb is required for the heat of vaporization. Minor adjustments were made to this calculation according to the details of the process. Because of the complexity of the system it was assumed that there is little opportunity for heat conservation in a multistage process.

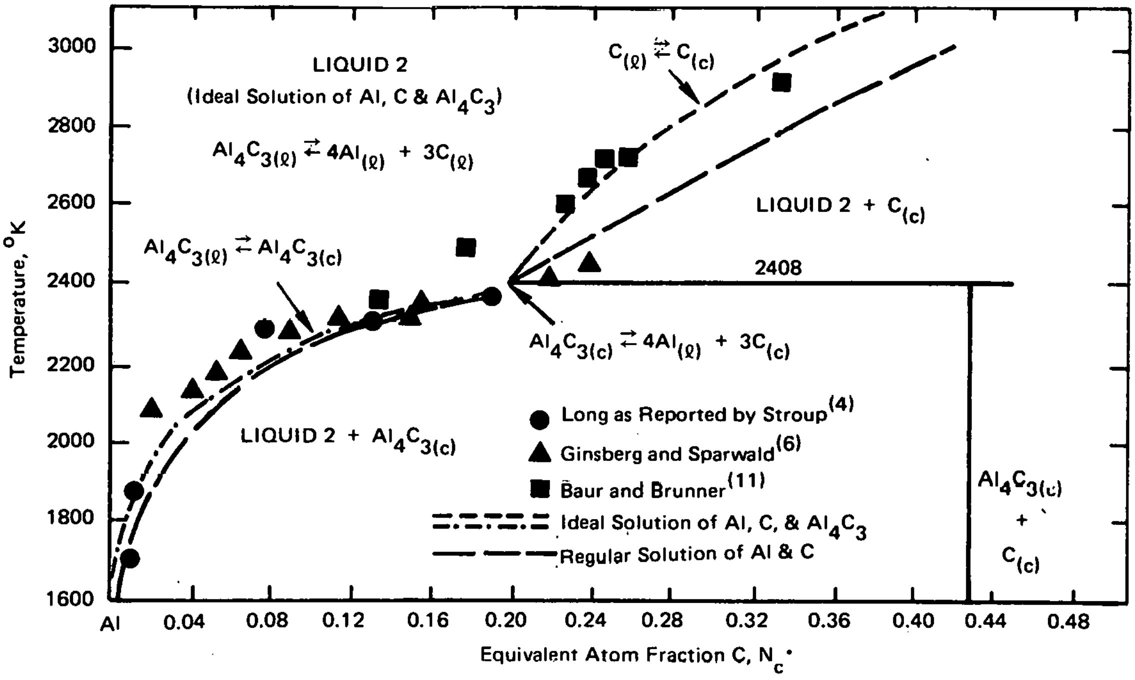


FIGURE 5 PHASE DIAGRAM FOR Al-C SYSTEM

Source: Cochran, U.S. Patent 3 971 653

TABLE 5

ELECTRICAL ENERGY REQUIREMENTS FOR DIRECT CARBOTHERMIC REDUCTION

Heat of reaction to Al(1)	5925 kcal/kg
Preheat of Al_2O_3	750
Preheat of coke	800
TOTAL	7475 kcal/kg

Assuming a furnace efficiency of 65% and a reaction efficiency of 80%, thermal energy requirements are

$$7457 \times \frac{1}{0.65} \times \frac{1}{0.8} = 14,375 \text{ cal/kg}$$

$$= 16.70 \text{ kWhr/kg}$$

$$= 7.58 \text{ kWhr/lb}$$

Source: Arthur D. Little Estimates

4.3 Selected Patents on Direct Carbothermic Reduction

U.S. Patent 2 776 884, Jan. 8, 1957; Grunert assigned to Pechiney.

In this process bauxite is heated with a sufficient amount of carbon to reduce the iron, silicon and titanium present and at the same time produce corundum (alumina). The two liquid layers formed are easily separated. In a second stage, the corundum is reduced with additional carbon at a temperature in excess of 2100°C. The aluminum and Al_2O distilled off are condensed in a tower of coke at 1700°C as Al_4C_3. The later is subsequently decomposed at 2000°C at a pressure of 20-50 mmHg. Using two towers which alternate between deposition and decomposition, it is possible to operate on a continuous basis.

The process is fundamentally sound but very complex; it is considered that the recovery of aluminum is likely to be inefficient with a high probability for contamination with iron and silicon. We have estimated the total electrical energy needs based on a two stage process to be in excess of 15 kWhr/lb of aluminum.

U.S. Patent 2 829 962, April 8, 1958; Miller, Foster, and Baker assigned to Alcoa.

A melt is formed from Al_2O_3 and C in such a ratio that a single phase of Al_4O_4C is formed. Additional carbon is added at a temperature of between 1900 and 2100°C such that the Al_4C_3 formed reacts with Al_4O_4C according to

$$Al_4O_4C + Al_4C_3 \rightarrow 8Al + 4CO$$

The aluminum, with some aluminum carbide, forms a new metallic phase. Controlled addition of the proper ratio of alumina and carbon ensures a continuous process. The aluminum carbide is removed from the aluminum by fluxing with chlorine. Plant details in the patent are scant but the precise delineation of stoichiometric ratios and temperatures indicate that a substantial amount of experimental work was carried out. We estimate the electrical energy requirements to be $\sim$ 10kWhr/lb.

U.S. Patent 2 974 032, March 7, 1961; E. Grunert, assigned to Pechiney.

The basis of this process is the high temperature arc (2400°C) reduction of a carbon-alumina charge of carefully controlled composition. Volatile components are condensed on the incoming charge. The aluminum and aluminum carbide are separated by fluxing in a sodium chloride melt at 800°C. Operating problems in the form of controlled addition of the charge and in the condensation process can be anticipated. The patent claims effective control by first preparing hollow spherical agglomerates of corundum and carbon in an electrothermal prereduction of an impure ore. From quantitative information provided in the patent, the electrical energy requirements of the arc furnace are 6.2 kWhr/lb of aluminum. Uniform temperatures and a very stable arc are claimed because of the ionization of alumimun in the gas phase - a feature not realized in submerged arc furnaces. Total energy requirements because of the preformation of corundum are estimated to be close to 10 kWhr/lb.

U.S. Patent 3 251 676, May 17, 1966; Johnson.

In this patent the production of aluminum is based on reduction of aluminum in the presence of an alloying component chosen from Fe, Si, Mo, Cr, V, Ti, Co, W, or Zr. The process takes advantage of the fact that the alloying component inhibits aluminum carbide formation thus simplifying the high temperature chemistry. The aluminum is subsequently obtained by distillation under vacuum. It is suggested in the patent that the latter process is assisted by the injection of magnesium vapor. A detailed description of a proposed design is given in the patent, but there is no indication of reduction to practice. Contamination with heavy metals and magnesium seems probable. We estimate that the electrical energy requirement is 8 kWhr/lb for the reduction process and 4 kWhr/lb for the distillation for a total of 12 kWhr/lb.

U.S. Patent 3 607 221, Sept. 21, 1971; Kibby assigned to Reynolds.

Very high temperatures (2400°C) are used in the reduction of alumina with carbon, the volatile gases are condensed into liquid aluminum at 2100°C percolating through a matrix of calcium oxide. Relatively low power requirements are cited, 6.5 kWhr/lb, but there are no practical details particularly with respect to inhibition of the back reaction between aluminum and carbon monoxide.

U.S. Patent 3 723 093, March 27, 1973; Tadahisa Shiba, assigned to Showa Denko.

This patent describes electric arc reduction of alumina with carbon at 2500°C, but in a furnace that is designed for local arc action. This is achieved by switching between electrodes in a multiple array, or by moving the furnace laterally or tilting it. It is claimed that in the cooler regions of the furnace (1400°C), aluminum carbide will solidify and that the aluminum may be tapped off. It is unlikely that the aluminum to carbon ratio can be controlled sufficiently well throughout the furnace to provide substantially carbide-free aluminum, also, there is no consideration of vaporization of Al and Al_2O nor of the back reaction. Power consumption is stated to be 4.5 kWhr/lb, but given the complexity of the operation, it is difficult to substantiate this figure.

U.S. Patent 3 929 456, December 30, 1975, Kibby, assigned to Reynolds.

This patent describes an arc furnace in which the heat input is limited by pulsing so that the aluminum produced moves out of the hot zone and is cooled on unreacted charge. In operation a yield of 64% is obtained from a carefully formulated charge, the product has less than 0.5% Al_4C_3. This process has not been operated on a scale larger than 100g quantities. We have estimated the energy requirements for a large scale process as 8 kWhr/lb.

U.S. Patent 3971 653, July 27, 1976; Cochran, assigned to Alcoa.

This patent document contains one of the most comprehensive discussions of the thermodynamics of the Al-C-O and Al-C systems. Based on an analysis of the data presented, a scheme is proposed based on two liquid phases at different temperatures but in contact. The intended configuration is best understood by examination of Figure 6. At the low temperature (2050°C) the reaction that takes place is the formation of Al_4C_3 according to

$$Al_2O_3(s) + 9C(s) \rightarrow Al_2O_3(l) + Al_4C_3(l) + 6CO(g)$$

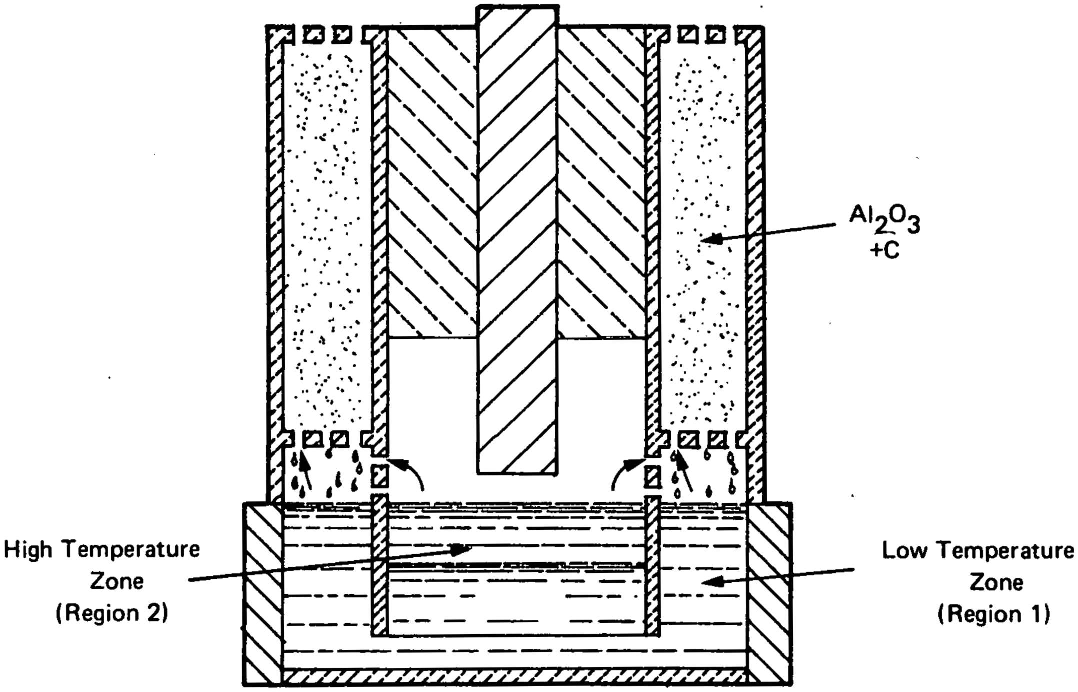
Migration in the liquid to region 2 at 2100°C results in the reaction

$$Al_2O_3(l) + Al_4C_3(l) \rightarrow 6\ Al(l) + 3CO(g)$$

The important aspect of the process is the elimination of much of the carbon monoxide associated with overall reaction before any aluminum is produced. Again aluminum or Al_2O vapors are condensed on the charge. There is still a requirement to separate aluminum carbide to obtain acceptably pure aluminum. Even so, careful control of the alumina-carbon ratio in the feed is necessary to avoid the presence of excess carbon in region 2. The process is conceptually sound though materials of construction and specific equipment design are not set out in the patent. The coexistence of the two liquids with a temperature differential minimizes the energy requirements but we still anticipate that the electrical energy required would be on the order of 8 kWhr/lb.

U.S. Patent 4033757, July 5, 1977; Kibby, assigned to Reynolds.

Magnetic fields are used to deflect a plasma to different regions of an alumina carbon charge as a means of limiting the total heat input to the charge. The claim is that any aluminum produced has the opportunity to move away from the hot zone prior to any significant vaporization. The carbide



Note: See U.S. Patent 3971653 for Details.

FIGURE 6. TWO–ZONE ARC FURNACE

content of the aluminum metal is said to be less than 10%. Another feature of the approach is that it is recommended that the feed be prereduced to form briquettes of Al_4O_4C. It would appear from the examples quoted that there is extensive bench experience of this process but there is no evidence of large scale operations. Electrical energy requirements are difficult to assess. Given thermal prereduction to the oxycarbide and good efficiency in the plasma furnace, we estimate that the figure could be as low as 6 kWhr/lb.

U.S. Patent 4049 425, September 20, 1977; Middlehoek, Santing and Dost, assigned to Shell.

Alumina or bauxite is reduced in the presence of iron, cobalt or nickel at reduced pressure to inhibit carbide formation. Alloys of up to 90% aluminum are claimed. There is no description of the furnace nor any indication of reduction to practice.

U.S. Patent 4099959, July 11, 1979; Dewing, Huni, Sood and Sontham, assigned to Alcan.

The basis of this patent is the formation of a working liquid consisting of 24% Al_2O_3 and 76% Al_4O_4C that is circulated between two zones, one at a temperature of 2000°C the other at 2090°C. Additional carbon and alumina are added separately such that at the lower temperature the reaction

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO$$

takes place and at the higher temperature, with addition of alumina, the reaction is

$$Al_4C_3 + Al_2O_3 \rightarrow 6Al + 3CO$$

The aluminum metal is tapped off and aluminum vapor and Al_2O formed by the back reaction with carbon monoxide are condensed on the carbon feed.

The patent describes electric resistance heating and several configurations for reactors, most of which have the common feature of a sloping interconnection between the two heat zones. The latter provides the opportunity to use the carbon monoxide generated in the reaction to act in a lift pump to induce circulation. The electrical resistivity of the melt with its high oxycarbide content should remain fairly constant so that the heat input can be carefully controlled. This makes for efficient operation and electric energy consumption estimated to be 8 kWhr/lb of aluminum.

4.4 Discussion of Direct Carbothermic Reduction

From information available at the present time, there are no fundamental thermodynamic or kinetic reasons to prevent the production of aluminum by direct carbothermic reduction. However, some of the high temperature kinetics are not very well defined and there has not been a production scale demonstration of any of the proposed approaches.

Process temperatures are very high and the reactants corrosive. This means a severe challenge and though it is possible to protect many surfaces with frozen melt this often means a compromise in thermal efficiency. Materials handling probably presents even greater problems, particularly since there is a need to control stoichiometric ratios on a local rather than an average basis. This aspect is aggravated by the fact that the oxidic melts are sticky and viscous. Closed furnace operation is also essential to exclude oxygen and to attain maximum thermal efficiency.

To reach the reaction temperatures it is necessary to use electric heat. Though burning excess carbon in oxygen might be acceptable from a temperature point of view, it becomes almost impossible to exercise control of the chemistry to the extent needed. (This is not true of alloy systems, for example, aluminum-silicon, in which the chemistry is less complicated; these are discussed in the next section.) The electrical energy requirement is in every case-according to our estimates-greater than that required in the Hall-Heroult cell operating under typical circumstances.

The overall conclusion must be that direct carbothermic reduction processes for the production of aluminum would not provide lower electrical energy consumption than the Hall-Heroult process, but should there be any reason that the latter practice could not be pursued, then a viable alternative approach exists. In the absence, in the distant future, of ready availability of carbon for anode fabrication, alternative technology might well be needed.

Under these circumstances we recommend a study program to define deficiencies in our knowledge on the thermodynamics and kinetics of direct carbothermic reduction and to identify potential materials of construction for reactors and ancillary components. Based on the findings, experimental programs should be initiated to expand our data base and ensure preparedness for any need for future change.

5.0 CARBOTHERMIC REDUCTION TO FORM ALUMINUM SILICON ALLOYS

5.1 Concept

Carbothermic reduction of alumina/silica mixtures is somewhat more straightforward than the reduction of alumina. The principal reason for this is that reduction of silica to silicon carbide takes place at 1600°C, a temperature considerably below that at which Al_4C_3 can be formed (2000°C). The aluminum silicon alloy is formed in a similar sequence of reactions to that for aluminum with SiC replacing the Al_4C_3.

$$3SiO_2 + 9C \rightarrow 3SiC + 6CO$$

$$2Al_2O_3 + 3C \rightarrow Al_4O_4C + 2CO$$

$$Al_4O_4C + 3SiC \rightarrow 4Al + 3Si + 4CO$$

The important difference is that the overall reaction may be carried out at 1950°C instead of 2100°C. This means less losses due to vaporization and given the proper kinetics no separation of a viscous glassy phase. The reactions can also be carried out in sequence to remove much of the carbon monoxide prior to metal formation.

The ratio of aluminum to silicon in the feed material is of obvious importance and should be close to two parts alumina to three parts silica. In practice this ratio may be achieved by blending of ores, though this is not necessarily a convenient and economic method of operation. It is also essential that the carbon content of the melt be close to the stoichiometric requirement, too little and there will be unreacted alumina, any excess will remain in the alloy phase.

5.2 Selected Patents

U.S. Patent 3257 1977, June 21, 1966; Schmidt, assigned to Reynolds.

This patent describes a method for producing an aluminum-silicon alloy in conformity with the principles set out above but with the additional feature of adding iron or titanium. The formation of intermetallic compounds in the liquid phase reduces the evaporation of aluminum and gives rise to a melt that is relatively easy to handle. On cooling, the intermetallic compound and elemental silicon crystallize out and can be separated by centrifugation. A 12% silicon in aluminum alloy is the final product, the yield of the alloy can be increased by processing the solids from the centrifugation process. The patent covers the stoichiometry of the process in close detail but there is no indication of its practice on a large scale. We estimate electrical energy requirements to be in excess of 12 kWhr/lb.

U.S. Patents 3661 561, 3661, 562, May 9, 1972; Trey, Hutchinson, Seth, Lanier, assigned to Ethyl Corporation.

These patents describe a blast furnace operation for the reduction of aluminum-silicon ores. The blast furnace is divided vertically into two zones, one containing only carbon, the other the ore and carbon. By blowing the carbon side with oxygen, carbon monoxide is generated at sufficiently high temperature to effect reduction in the second zone. There is no evidence of testing as a large scale process.

U.S. Patent 3758 289, September 11, 1973; Wood, assigned to Ethyl Corporation.

A two-step reduction is claimed in this patent; an initial reduction with a fossil fuel, in which temperatures of 1500-1800°C are reached, is followed by electric arc reduction at 2000-2300°C. This appears to be a useful dual approach with the merit of reduced electrical energy consumption together with good stoichiometric control. However, the main energy requirement is for the endothermic reduction process (4 x greater than the preheat) that is an electrical energy demand. Again, there is no evidence of large scale practice. We estimate the electrical energy requirements to be at least 6 kWhr/lb.

U.S. Patent 4046 558, September 6, 1977 and 4053 303, October 11, 1977; Cochran, Das, Milito, assigned to Alcoa.

These patents also describe ranges of chemical composition and stoichiometries for reduction to an aluminum-silicon alloy. The important difference, however, is that the reactions are driven thermally by the combustion of excess carbon with oxygen. To avoid excessive losses associated with the vaporization of aluminum at the higher temperatures the overall reaction is carried out in stages.

$$3SiO_2 + 9C \rightarrow 3SiC + 6CO \text{ at } 1500\text{-}1600°C$$

$$2Al_2O_3 + 3C \rightarrow Al_4O_4C + CO \text{ at } 1600\text{-}1900°C$$

$$Al_4O_4C + 3SiC \rightarrow 4Al + Si + 4CO$$

Approximately two-thirds of the reactive carbon monoxide and a significant amount of the combustion carbon monoxide is removed from the system before there is any production of aluminum metal. Control of feed rates of ore and carbon are critical if proper stoichimetry is to be maintained.

The striking advantage of this process is that electrical energy demands are minimal. We estimate the thermal energy requirements based upon 55% thermal efficiency and 80% completion of the reduction process to be 70 x 10^6 BTU/ton of aluminum. The equivalent figures for electric furnace operation are 217 x 10^6 BTU/ton, a figure that reflects a thermal to electric energy conversion efficiency of 34%. This makes the direct thermal reduction to the aluminum silicon alloy particularly attractive energetically, it becomes even more attractive when it is realized that there are sixteen tons of low BTU gas (carbon monoxide) produced with every ton of aluminum. Selective cleaning and leaching of the ores before firing may be necessary. Also, the process demands a high purity carbon source, at present metallurgical grade coke is proposed.

5.3 Discussion

The lower temperatures required to produce the metallic phase in the aluminum silicon system bring it within the realm of direct reduction in a blast furnace if oxygen or oxygen enriched air is used. By avoiding the heat to electrical energy conversion inefficiency, this approach must show a distinct advantage over electric furnaces. There is still a need for special techniques in material handling (in the phased reaction approach the viscous oxycarbide is formed in the second stage) and in reducing vaporization losses. The biggest problem appears to be control of the carbon-oxidic ore ratio. It could well be that the dual approach with electrical heating for the final step of the process would provide the opportunity for fine tuning the process.

Because there is a large potential market for aluminum-silicon casting alloys, this concept is extremely attractive as an energy saver. We recommend that studies of the Al-Si-C-O system be continued vigorously and that the technical and economic aspects of a large-scale process be fully explored.

6.0 THE SUBCHLORIDE PROCESS FOR THE PRODUCTION OF ALUMINUM

6.1 Concept

The subchloride or Gross process for the refining of aluminum has probably been the most intensively pursued of the non-electrolytic processes. The basis is that at high temperatures aluminum chloride ($AlCl_3$) in the vapor phase will react with aluminum metal to form the volatile monochloride or subchloride ($AlCl$) according to

$$AlCl_3 + 2Al \rightarrow 3AlCl$$

This reaction is almost complete at 1300°C. When the subchloride is cooled, the reaction is reversed with aluminum chloride and aluminum vapor being formed in a highly exothermic reaction.

$$3AlCl \rightarrow 2Al + AlCl$$

The process consists of the reduction of an impure ore, typically bauxite, to give aluminum metal alloyed with silicon and to a lesser extent iron and titanium. The reduced ore is exposed to aluminum chloride in a converter so that the aluminum alone is distilled off as the subchloride. When the subchloride is condensed, aluminum metal is recovered and the aluminum chloride recycled.

6.2 Process Engineering

The impure alloy that is fed to the converter is produced from bauxite that is first calcined and sintered in a rotary furnace with coke. The sinter is then reduced with coke in a closed submerged arc furnace of the type used to produce ferrosilicon of ferromaganese. The impure alloy in the form of a granular solid is transported to the converter, an electrically heated shaft furnace in which the charge is moving continuously. Since the charge constitutes the resistive load of the furnace and has a large negative coefficient of resistance it is preheated with external resistance heaters and by partial condensation of monochloride vapors to effect better furnace control. The convertor, as built and tested by Alcan, was a reactor 50' high and 4' in diameter, details of its construction are given in the patent literature.

The monochloride produced in the converter passes with unreacted aluminum chloride into a decomposer, a splash condenser with liquid aluminum as the working fluid. The decomposition is a highly exothermic reaction producing an extremely corrosive material so that the splash condenser can be considered an elegant approach to a difficult practical problem. Heat is removed from the aluminum metal with a sodium chloride - aluminum chloride molten salt mixture. There is also a second stage of condensation in which the aluminum chloride is condensed. This too is a splash condenser with the sodium chloride-aluminum chloride melt as the cooling fluid. This melt is recycled via the first condensation stage and a heater to the converter. The pressure developed in the recycling process is responsible for the circulation of aluminum chloride through the system, i.e., no pumps are needed.

All the components of this system were built and tested by Alcan, details are given in the patents, the more important ones are listed in the Bibliography.

The flowsheet for the process as defined by Alcan in the patent literature is set out in Figure 7.

6.3 Energy Requirements

Alcan was able to develop a well defined energy and mass energy and mass balance for the subhalide process. The figures are presented in Table 6. It is interesting to note that the conversion operation consumes as little electrical energy as 2.1 kWhr/lb but that the initial reduction process, despite the high technology, required 6.5 kWhr/lb. The total of 8.6 kWhr/lb ends up in excess of the Hall-Heroult requirements for electrical energy of 6-7 kWhr/lb. This was the principal reason for Alcan abandoning the project; it was claimed that most technical problems had been solved to their satisfaction. The prospects for reducing energy consumption in the electroreduction step are not good, so that the overall process, as described, is not atrractive as an alternative to the Hall-Heroult process.

If, however, the first step were a thermal reduction process, then there is apparently a viable system since the electrical energy for the subchloride step is just over 2 kWhr/lb. We recommend, as an adjunct to the proposed analysis of thermal reduction to the aluminum-silicon alloy, a detailed examination of the feasibility of pure aluminum production from the alloy using the subchloride process.

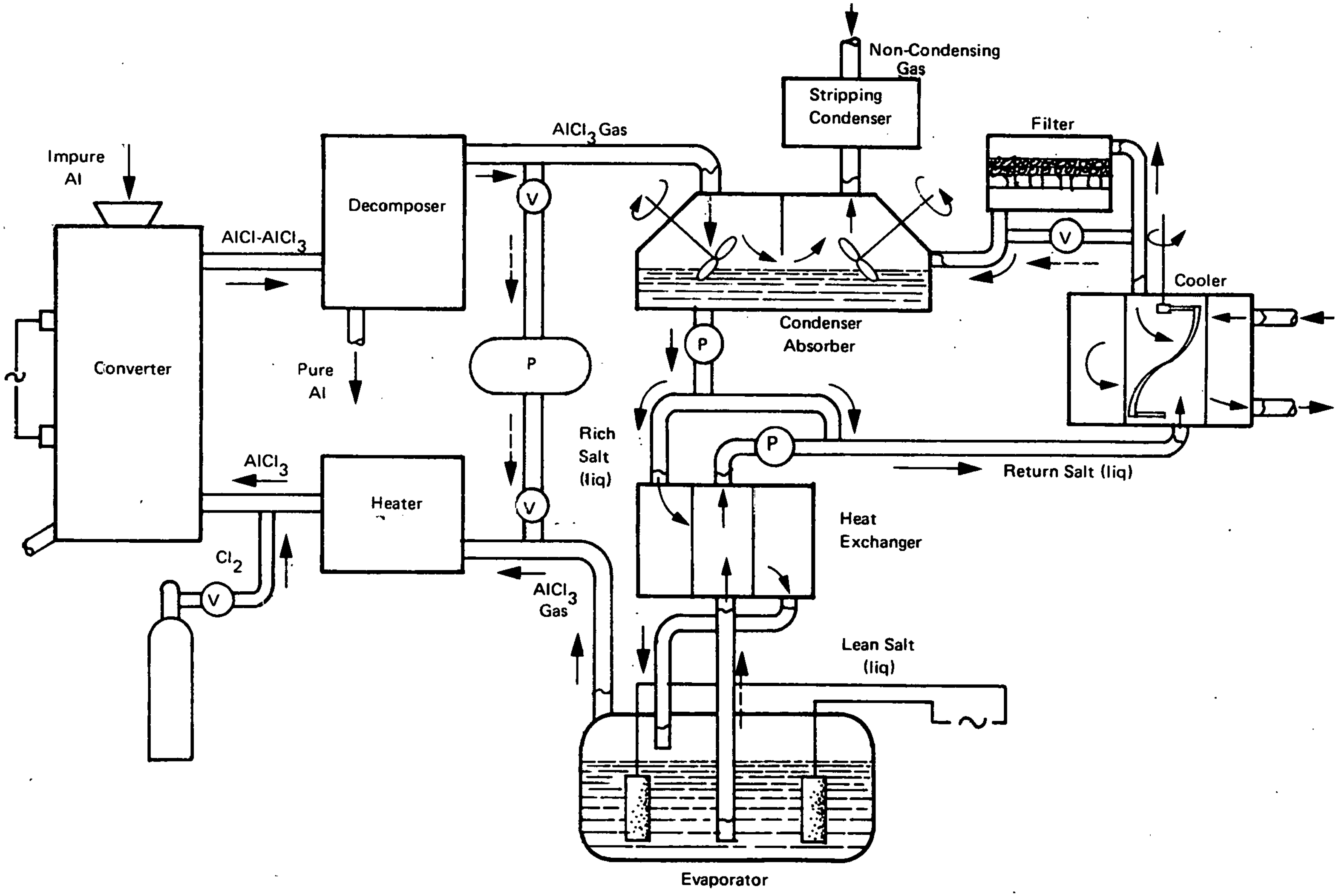


FIGURE 7 FLOWSHEET FOR THE SUBCHLORIDE PROCESS

Source: NWF Phillips et al U. S. Patent

TABLE 6

Mass and Energy Balance for the Alcan Subchloride Process

Raw Materials and Fuels	lb/lb Al
Bauxite (60% Al_2O_3)	3.6
Anthricite	0.3
Bituminous Coal	1.8
Soderberg Paste	0.08
Chlorine Make Up	0.01
Energy Consumption	kWhr/lb
Reduction	
Sintering	0.041
Coking	0.008
Furnace	6.380
Auxilliary	0.032
Distribution	0.066
	6.527
Refining	
Operations & Losses	2.137
Total	8.664

Total Thermal Energy Equivalent 247 MBTU/ton

Source: Private communication, N.W.F. Phillips.

7.0 DISPROPORTIONATION OF ALUMINUM SULPHIDE (Al_2S)

7.1 Concept

The subsulphide process though similar in concept to the subchloride process has one important difference - there is no requirement for prereduction of the oxide. Initially, the trisulphide Al_2S_3 is reacted with alumina and carbon to produce the volatile subsulphide.

$$2Al_2O_3 + Al_2S_3 + 6C \rightarrow 3Al_2S + 6CO$$

This reaction will take place at 1000-1200°C at a pressure of 5 mmHg or up to 2000°C and atmospheric pressure. A practical compromise is probably 1800°C at 50 mmHg. When the subsulphide is cooled, it disproportionates to aluminum metal and the trisulphide

$$3Al_2S \rightarrow Al_2S_3 + 4Al$$

Both the aluminum and the trisulphide are condensed rapidly to minimize the back reaction between aluminum and carbon monoxide. The aluminum is recovered by remelting at 700°C. The melting point of aluminum sulphide is 1100°C though there is significant solubility of the sulphide in the aluminum at 700°C, resulting in some contamination.

Thermodynamic data on the Al-C-O-S system are limited (8) but it is generally agreed that the process proposed by VAW based on subsulphide formation is sound. It has the advantage over the subchloride system that there is no requirement for prereduction of the bauxite. Operating temperatures for practical production rates, however, would probably need to be significantly higher, perhaps 1800°C compared to 1300°C for the subhalide process.

7.2 Energy Requirements

The VAW patent (9) claims that the electrical energy requirements for this process are significantly less than that of the Hall-Heroult process (cited by VAW as 8 kWhr/lb). However, the overall reaction, despite the sulphide intermediate is still the reduction of alumina with carbon so that the overall heat of reaction is the same as other carbothermic processes. Since this heat of reaction varies little with temperature the energy requirement would not be significantly different from that calculated in Table 5. The heat of sublimation of Al_2S must also be added to this. From the heats of formation the heat of reaction for the formation of Al_2S is 9080 kcal/kg (compared to 5925 kcal/kg for the reduction of Al_2O_3) from which we can calculate the electrical energy requirements for

75% thermal efficiency and 80% reaction efficiency to be 10 kWhr/lb.

There is no report of the subsulphide process being satisfactorily practiced on a large scale. Operating under reduced pressure at very high temperatures on an industrial scale is extremely difficult and expensive. There must also be problems in handling the trisulphide which is easily hydrolyzed. A further factor is the extent of trisulphide contamination of the product aluminum. This will convert to alumina at the surface to the detriment of the physical characteristics of the metal. We do not consider this process to be a practical approach to aluminum production.

8.0 ALUMINUM PRODUCTION THROUGH AN ALUMINUM NITRIDE INTERMEDIATE

8.1 Concept

Aluminum will form a nitride according to the reaction

$$2Al + N_2 \rightarrow 2AlN$$

The reaction starts to take place at 400°C but does not proceed to completion until temperatures of 1800-1900°C are attained. The nitride sublimes above 2000°C and may most easily be decomposed by reducing the pressure at this temperature.

In concept the reversibility of this process offers the opportunity for producing aluminum, particularly when it is realized that the following reaction

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

can take place at about 1500°C.

8.2 Patent Coverage

U.S. Patent 2,835,566 May 20, 1958; Pierieres and Ruell assigned to Pechiney.

In this process the first step is the production of AlN which is sublimed from bauxite reduced with carbon in nitrogen. The end product contains alumina from the volatile suboxide formed according to

$$3Al_2O \rightarrow Al_2O_3 + 4Al$$

and aluminum carbonitride also formed from the suboxide

$$Al_2O + 3C + N_2 \rightarrow 2AlCN + CO$$

The patent deals primarily with the conversion of the crude nitride to pure aluminum. This is achieved by decomposition of the nitride at 1700°C at 0.5 mm Hg pressure in an induction furnace. The carbonitride is collected on the surface of a trap held at 1500°C where it is converted to the carbide according to

$$3AlCN + 4Al \rightarrow Al_4C_3 + 3AlN.$$

The surface of the trap is cleaned periodically by raising the temperature, this reverses the above reaction to vaporise the carbonitride which is collected in a disposable condenser. The suboxide is also removed by deposition on a disposable surface held at 1000°C. Aluminum metal is collected in the lower section of the reactor.

8.3 Discussion

This is a complex, batch process for the production of aluminum that does not appear to have any particular merit. We have not made an analytical study of the energy requirements since they are obviously significantly greater than those of the Hall-Heroult process.

9.0 ALUMINUM PRODUCTION BY CHLORIDE ELECTROLYSIS

9.1 Concept

Aluminum may be obtained by the electrolytic decomposition of aluminum chloride in a fused chloride melt. This process has been developed by Alcoa (The Alcoa Smelting Process-ASP) to the stage where a demonstration plant with a capacity of 15,000 tons per year has been operated for several years. The capacity is being expanded to 30,000 tons per year as improved technology, particularly in aluminum chloride production, is put on stream.

The process consists of the chlorination of Bayer aluminum to form aluminum chloride which is then decomposed in a multi electrode cell of bipolar configuration to form aluminum and chlorine. The electrolyte is approximately equimolar sodium and lithium chlorides with about 5 mole % aluminum chloride at a temperature of 730°C. The major advantage of the process is its low specific electrical energy consumption at 4.5 kWhr/lb. This low value can be attributed primarily to the close spacing (0.25") of the non-consumable, bipolar electrodes. In the Hall-Heroult cell, the anode-cathode distance is between 1.0 and 2.0" with an associated voltage loss of 2.0V. In the ASP, the ohmic losses in the electrolyte correspond to the less than 0.5V of the cell operating voltage.

9.2 Process Engineering

The various stages of the ASP are shown in the flow diagram in Figure 8. Details of the components are available in the patent literature. A list of the more important patents is given in the bibliography, a brief description of the process is given below.

The raw material for the ASP is Bayer alumina with stringent specifications on impurities, see Table 7. The chlorination step requires carbon as a reducing agent; in practice the alumina is impregnated with carbon in a two stage fluid bed system fired with No. 6 fuel oil. The top stage is operated at a relatively low temperature on which unburned fuel oil can be condensed on the alumina feed to the lower stage at 900°C. In the lower stage, the fuel oil is cracked and coked. The feed rate is adjusted such that the amount of carbon deposited is slightly more than the stoichiometric requirement to reduce the oxide to form carbon dioxide.

Two methods for chlorination are described in the patent literature. The first is a fluidized bed, operated at 590°C in which the aluminum is converted primarily to aluminum chloride. Minor but significant amounts of hydrogen chloride, aluminum

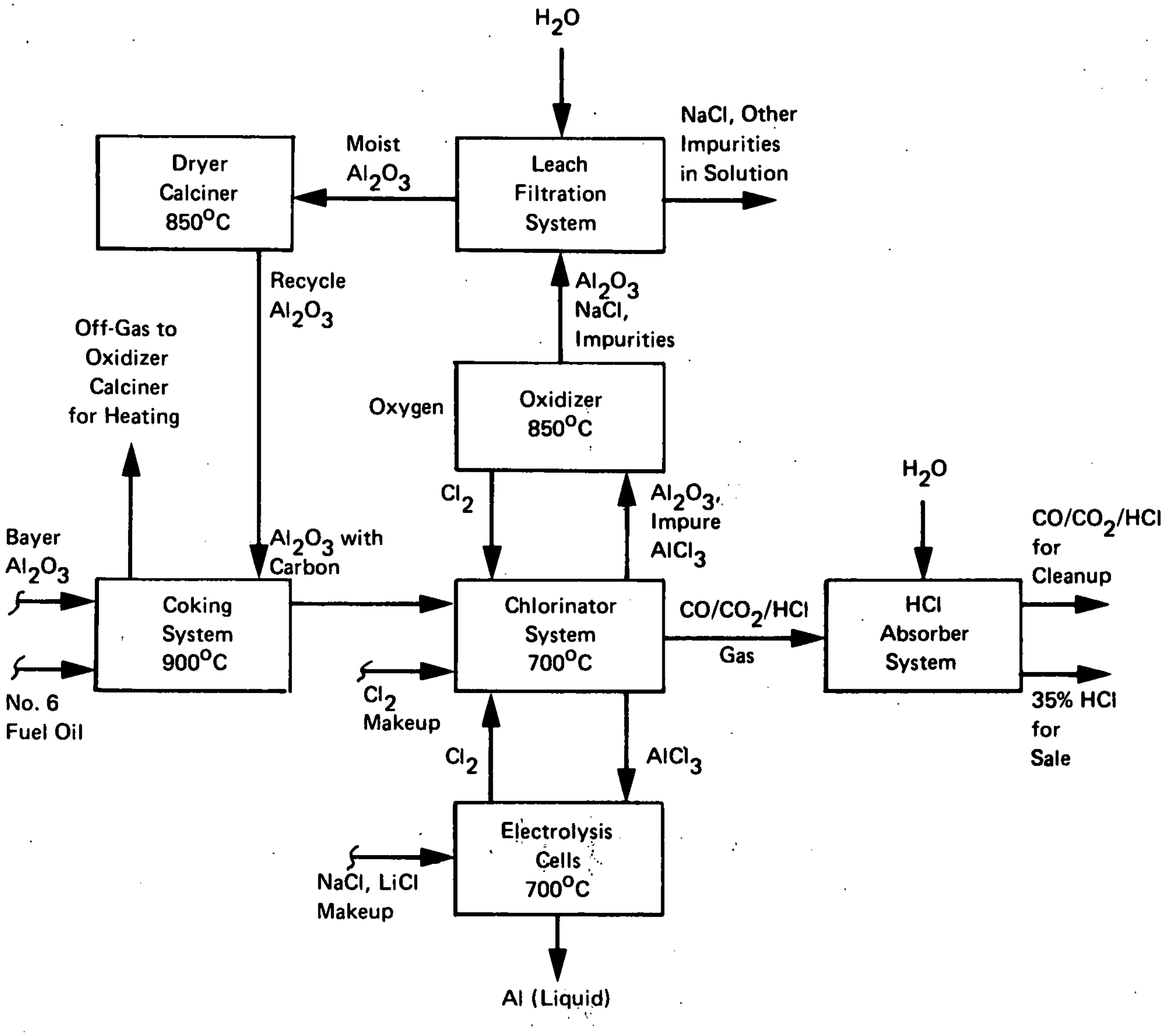


FIGURE 8. FLOWSHEET FOR ALCOA SMELTING PROCESS

TABLE 7

Specification for the Alumina Feed for the Alcoa Smelting Process

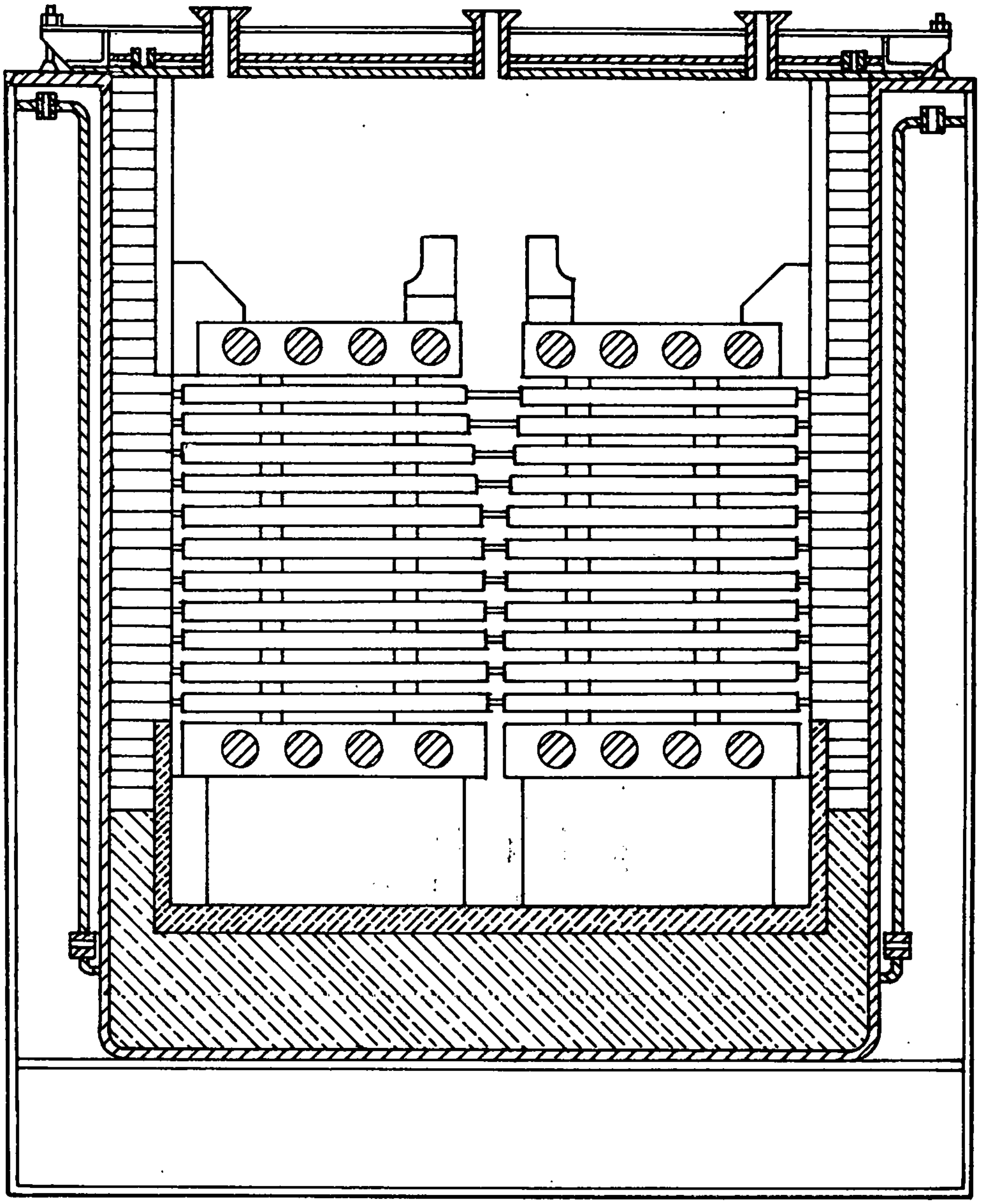
Al_2O_3	99.426% min
SiO_2	.025 max
Fe_2O_3	.03 max
CaO	.06 max
MgO	.002 max
NiO	.005 max
CaO	.01 max
MnO_2	.002 max
Na_2O	.4 max
TiO_2	.005 max
ZnO	.02 max
V_2O_5	.002 max
Cr_2O_3	.002 max
K_2O	.005 max
Li_2O	.001 max
P_2O_5	.005 max

hydroxychloride, aluminum oxychloride and sodium chloride are also produced. The sodium content is derived from the alumina in which it is present as an impurity from the Bayer process.

A two stage condensation process, removes unreacted alumina and carbon, the oxychlorides and sodium chloride. The condensate is oxidized to regenerage chlorine, the sodium chloride washed out and the alumina recycled to the first stage of the process. The aluminum chloride is subsequently condensed in a fluid bed at 65°C. The hydrochloric acid which is not condensed is removed in an absorption column to provide a useful byproduct.

In the second process, the chlorination is carried out in a molten salt bath, typically 70% aluminum chloride, 30% sodium chloride in the temperature range of 780 to 815°C. Cuprous or cupric chloride is added to the bath as a catalyst. Bayer alumina and brushed coke are fed to the bath through which chlorine is bubbled from the bottom. Carbon monoxide is claimed to be an effective alternate reductant. The oxychlorides and sodium chloraluminate are condensed from the aluminum chloride vapor as in the previously described method.

The aluminum chloride is fed to the electrolytic cell where it dissolves rapidly in the lithium-sodium chloride electrolyte. The cell is shown in section in Figure 9, a detailed description of the components, is given in the patent literature. Each cell consists of twenty to thirty bipolar carbon electrodes stacked horizontally. The upper surface of each electrode is a cathode on which aluminum is produced. The chlorine formed on the lower surface moves in channels towards a central space where it circulates electrolyte by a gas lift action. This circulation of electrolyte sweeps the aluminum off the cathode so that it falls to the sump and does not collect on the surface. This means that a small interelectrode spacing can be used. The cell design and electrolyte flow patterns are essential to high current efficiency. Electrolyte circulation also ensures an adequate supply of aluminum chloride throughout the cell. This is important because a local deficiency of aluminum chloride results in the deposition of an alkali metal which can destroy the graphite surface by forming an intercalation compound. This is particularly true of potassium and every effort is made to keep the potassium content of the bath as low as possible. Though aluminum chloride is highly soluble in the melt, in practice, the concentration is kept below 10 wt % and preferably closer to 6.5 wt %. The disadvantages of the higher concentration are lower conductivity, higher viscosity, more recycle and potential attack of the refractory lining of the cell.



Note: Detailed description in U.S. Patent 4133727.

FIGURE 9. ALCOA SMELTING PROCESS BIPOLAR CELL

An essential aspect of cell operation is the complete exclusion of moisture and oxide species from the cell (hence the careful purification of the aluminum chloride). There are two problems associated with the presence of oxides, one is sludge formation, the other is consumption of the anode face of the graphite electrodes. There is every indication that Alcoa has these problems under complete control.

9.3 Comments on the Alcoa Smelting Process (ASP)

As already noted the major advantage of the ASP is a lesser requirement for electrical energy (4.5 kWhr/lb) than the Hall-Heroult process (6-8 kWhr/lb). A comparison of the two processes is given in Table 8. It is apparent that the major advantage of the ASP is the smaller anode-cathode separation, an advantage that more than offsets the higher reversible decomposition voltage of the chloride and slightly lower conductivity of the choride melt. The thermal energy associated with the chlorination process is slightly greater than that expended in the manufacture of prebake anodes.

The overall assessment of the ASP is that it is a technically viable process that represents an alternative technology to the Hall-Heroult process. The ASP technology is more sophisticated than Hall-Heroult so that the potential for down-time or periods of low current efficiency are inevitably greater. Current efficiency is very dependent on the maintenance of optimum hydrodynamic flow in the cell. Alcoa has studied this extensively and can maintain high efficiency on a routine basis. Thermal management and condensation of the volatile components of the electrolyte have also been extensively studied and do not now represent operational problems. The key to trouble free operation appears to be the purity of the aluminum chloride feed, oxides cause sludge formation and carry-over of sodium chloride slowly changes the composition of the bath. The patent literature contains many descriptions of processes and devices to insure aluminum chloride of at least 99.9% purity. One other major operational advantage over the Hall-Heroult process is the capability of the ASP to survive power failure.

We have recently made an estimate of the operating costs for the ASP, these are set out in Table 9. In arriving at these costs we have assumed that the fixed capital investment is the same as for a conventional plant (with prebaked anodes) of the same capacity.

TABLE 8

COMPARISON OF ASP AND H-H CELLS

	ASP	H-H
Current Density A/in^2	5-15	5-7 at the anode 2-4 at the cathode
Anode Cathode Distance in	0.25	1.5-2.0
Reversible Decomposition Voltage V	1.8	1.2*
Anode polarization V	0.4	0.5
iR losses in electrolyte V	0.5	2.0
Voltage per cell **	2.7	3.7

* Includes depolarizing action of carbon anode

** Practical cell voltages cannot be compared because of the ASP multicell bipolar stack configuration. Also note that these figures do not correlate directly with the practical values of kWhr/lb cited for the two processes unless assumptions are made about the current efficiencies.

TABLE 9

ESTIMATED COST OF PRODUCING PRIMARY ALUMINUM BY THE ALCOA SMELTING PROCESS

Annual Capacity - 160,000 Short Tons/Year
Capital Investment - 340,000,000

Raw Materials	Units	$/Unit	Unit/Ton	$/Ton	
Aluminum	Tons	140	1.930	270.20	
Oxygen	Tons	39	.020	.78	
Sodium Chloride	Tons	32	.001	.03	
Lithium Chloride	Tons	2100	.001	2.10	
Chlorine	Tons	125	.190	23.75	
					296.86
Utilities					
Fuel No. 6 - Fuel Oil	MMBTU	2.30	24.85	57.16	
Power	kwh	.015	10,500	157.50	
Water Process	M Gal	.50	0.200	.10	
Cooling		.05	100.000	5.00	
					219.76
Labor					
Operating and Maint.	man hrs	12.45	7.000	87.15	
Supervision and Adm.	man hrs	17.70	2.070	36.64	
					123.79
Operating Supplies					2.00
Maintenance Materials and Supplies - 1% of Capital Investment					21.25
Plant Overhead @ 50% of Labor					61.90
TOTAL PRODUCTION COSTS BEFORE DEPRECIATION AND GS&A					725.56
					36¢/lb

10.0 ALUMINUM PRODUCTION BY THE ELECTROLYSIS OF ALUMINUM SULPHIDE (Al_2S_3)

10.1 Concept

Aluminum sulphide can be decomposed by electrolysis in a cryolite or chloride fused salt bath to give aluminum and sulphur according to the overall reaction

$$2Al_2S_3 \rightarrow 4Al + 3S_2$$

Since the theoretical open circuit voltage for this reaction is 1.14V, comparing favorably to the 1.8V for the decomposition of the chloride, it would appear to lend itself to an energy efficient smelting process. Though some experimental work has been carried out there is no documented evidence of pilot scale or larger plants. We therefore have to make an assessment of the practicability of the process which depends on two main factors. The first is the degree of difficulty associated with the manufacturer of the sulphide according to

$$Al_2O_3 + 3/2\ S_2 + 3C \rightarrow Al_2S_3 + 3CO$$

The second is the current efficiency of the electrolytic step which can be impaired by the formation of a soluble monovalent aluminum sulphur complex at the cathode (10). Since this complex can be oxidized at the anode the current efficiency is lowered.

10.2 Practical Considerations

The preparation of the sulphide from alumina is a difficult reaction (11), there are no reliable data to establish whether the reaction will go to completion and whether the kinetics are fast enough for an economical large scale process. The reaction temperature will need to be in excess of 1100°C (the melting point of the sulphide) and in all probability electrical heating will be necessary. If we use the chlorination step of the subchloride process as an analogy, the energy requirements are equivalent to approximately 2 kWhr/lb of aluminum produced.

In the electrolytic step, if the voltage losses are comparable to chloride electrolysis, the cell operating voltage, based on the theoretical open circuit voltage of 1.14V, would be approximately 2.0V. This would correspond to an energy consumption of 3.3 kWhr/lb for a current efficiency in the range 85-90%. However, it is thought that this figure will not be achieved in practice because of the presence of the monovalent species. If we assume that the practical trade-off between ohmic losses and losses due to diffusion of the monovalent cation across the cell leads to a current efficiency of 75% then the energy consumption would be 4.0 kWhr/lb.

10.3 Discussion

It would appear from the above that the total electrical energy consumption associated with the production of aluminum from alumina through sulphide electrolysis is in the range of 5.3 to 6.0 kWhr/lb. This is sufficiently attractive to warrant experimental studies to better understand this process and define its real utility.

11.0 ALUMINUM PRODUCTION BY THE ELECTROLYSIS OF ALUMINUM NITRIDE

11.1 Concept

The key to aluminum production by electrolysis of aluminum nitride is the solubility of the nitride in a mixture of lithium nitride and lithium chloride. Though aluminum nitride is insoluble in cryolite and fused chlorides, it will dissolve in the presence of lithium nitride to form a viscous melt probably containing complex ions corresponding to $Li_3N.3AlN$ (11). The attractive feature of nitride electrolysis is the low decomposition voltage, 0.79V at 727°C. However, the electrolysis process is a complex one that has not been studied very extensively.

11.2 Practical Considerations

In work carried out at Battelle, Geneva, (11) no aluminum was obtained on electrolysis until the bath had aged significantly. Analysis of the bath showed that the Li_3N content had dropped to 0.28 mole %, down from 12.5 mole % as initially formulated. When aluminum was deposited, it was found that the Faradaic efficiency was low but that it increased with increasing current density. At the present time, it is not known whether the low Faradaic efficiency is due to lithium deposition or the solubility of aluminum in the melt. At an operating voltage of 2.2V, however, the Faradaic efficiency was found to be close to 90%. Taking these factors into account, we may calculate the energy consumption for aluminum production. For the electrolytic step, we estimate this as 3.6 kWhr/lb. This and comparable figures for the Hall-Heroult and Alcoa processes are shown in Table 10.

In addition to the ill-defined electrolytic step, two other aspects of the overall production process present difficulties. These are the slow rate of dissolution of the nitride and the actual formation of the nitride. The former is a design and operating problem, but the latter is a more fundamental problem. Direct formation in a carbothermic reaction according to

$$Al_2O_3 + 3C + N_2 \rightarrow 3CO + 2AlN$$

is difficult. The reaction does not go to completion, and the carbonitride is formed as a byproduct. The problems associated with these factors are discussed in detail in Section 8. There is, however, an alternative route to produce the nitride by the reaction between aluminum chloride and ammonia.

$$AlCl_3 + NH_3 \rightarrow 3HCl + AlN$$

The complete scheme for the production of the metal with alumina as the starting material is shown in Figure 10. The hydrochloric acid is used to regenerate chlorine either by oxidation (Deacon process) or electrolysis. Despite the apparent com-

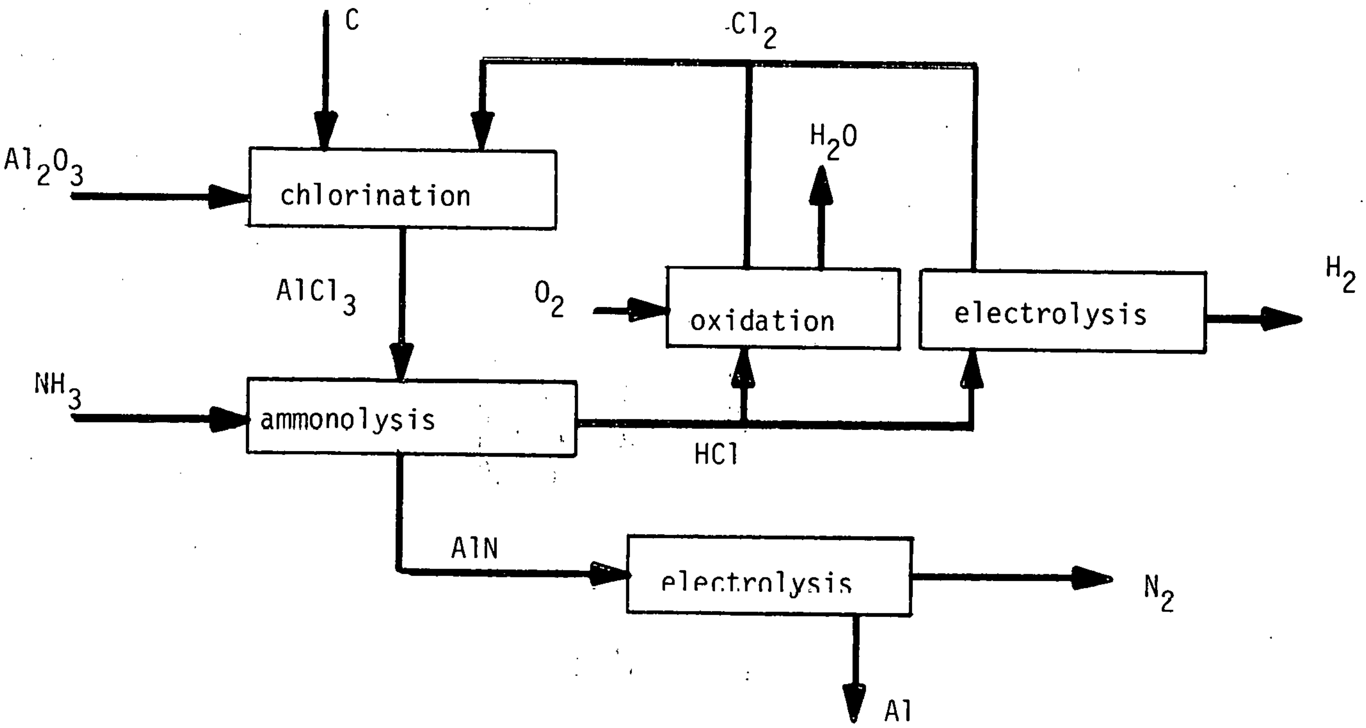
TABLE 10

Comparison of the Energy Requirements of AlN Electrolysis with ASP and H-H

	AlN	ASP	H-H
Electrical energy kWhr/lb	3.6	4.5	6.0-8.0
Total Thermal Energy 10^6BTU/ton	96	130	150-190
Energy equivalent to NH_3 10^6BTU/ton	36		
Total 10^6BTU/ton	132	140	150-190

FIGURE 10

AlN CONCEPT FLOW CHART



plexity of the system, it can be considered competitive with the Hall-Heroult and Alcoa processes. A breakdown of the equivalent thermal energy requirements for each process is given in Table 10 the figures for AlN were derived from the Battelle data. Note that the AlN and $AlCl_3$ figures include the thermal energy of the chlorination step.

11.3 Discussion

Nitride electrolysis remains of significant interest because of its low electrical energy requirements. In this context, more should be learned about the electrolytic step, particularly the long term stability of the electrolyte.

12.0 ALUMINUM PLATING FROM NON-AQUEOUS SOLVENTS

Aluminum is easily plated from many non-aqueous systems so that there is an opportunity for metal refining. Typical examples are:

- aluminum bromide in ethyl bromide
- aluminum chloride and ethyl pyridinium bromide in toluene
- aluminum chloride and lithium aluminum hydride in ether or tetrahydrofuran
- aluminum bromide and potassium bromide in toluene.

These baths are effective in producing hard lustrous deposits suitable as protective coatings and even for quite large electroformed structures. Without exception, the current densities used are low, and the current efficiencies fall with increasing current density. Typically, a bath with a current efficiency of 100% at 10 mA/cm^2 will be down to 40% at 30 mA/cm^2 (12). Accumulation of the products of the anodic process and side reactions degrade the performance of the bath in the form of increased resistance and also affect the quality of the aluminum deposit.

The non aqueous solvent systems are also quite resistive and do not offer the opportunity for dramatic energy savings. It is also considered unlikely that the chemistry can be modified to obtain any significant increase in rate. We do not recommend any studies in this area.

13.0 MAJOR IMPROVEMENTS TO THE HALL-HEROULT PROCESS

13.1 Basic Hall-Heroult Technology

Present day Hall-Heroult cells operate in the range of fifty to hundreds of kA. Large cells are preferred for their better economics, but there is an upper limit to their size defined by the capability to control the magnetically induced surges in the aluminum cathode. Because of these very large currents, it becomes very important to minimize voltage losses in the system. A breakdown of the losses in a typical prebaked anode cell is given in Table 2. The largest loss is in the resistance of the electrolyte (1.9V). The polarization associated with the electrochemical process is 0.5V, since the reversible voltage for the overall reaction is 1.2V.

13.2 Practical Considerations

Since the electrolyte composition has been optimized over the years, particularly with the addition of lithium carbonate to improve the conductivity, the primary factor in the control of this source of voltage loss is the anode cathode distance (ACD). This in turn is dependent on the consumption and repositioning of the anode and the depth of the aluminum pad which is drained at intervals. The ACD is, therefore, continuously varying usually between 1.0 and perhaps 2.25", though in some newer cells, the spacing might be slightly less. It should also be noted that the ACD in a cell is not uniform though gross variations tend to be self correcting.

Consideration of the above factors points to two approaches that provide the opportunity to reduce the ACD, one is to eliminate the need to accumulate an aluminum pool cathode, the second is to deploy a nonconsummable anode that can be permanently positioned.

13.3 Titanium Diboride Cathodes

The reasons that an aluminum pool is maintained as the cathode are that the liquid metal does not wet the carbon cathode, and that the electrode reaction is less efficient on the carbon surface. The search for alternative materials to carbon dates back to the 1950's, and it appears that the only candidate today is one of the early ones examined - titanium diboride. Much has been learned about its manufacture, particularly the requirement to avoid intergranular oxygen. (The molten aluminum attacks the oxygen and brings about physical degradation.) Titanium diboride has the advantage of being wet by molten aluminum and has demonstrated, in the laboratory, sufficient resistance to chemical attack. From the laboratory experiments, it is projected that a tile 1/4" thick would have a life of 7-8 years in a Hall-Heroult cell. In practice, no one has demonstrated sufficiently long life and reliability to undertake the risk associated with retrofitting a significant number of production cells. It is estimated that between two and three years of cell life are needed to justify the installation of TiB_2 cathodes.

The energy savings to be realized by reduction of the ACD to a range of 1/2" to 1" may be estimated to be close to 20% of typical existing cells. In practice it might prove to be more beneficial to increase production at the same energy consumption level rather than take advantage of the energy savings. To some extent there are operational constraints related to cell operating temperature and crust thickness that prevent direct saving of electrical energy.

Despite the closer spacing of the electrodes, the extent of the back reaction between aluminum and carbon dioxide to regenerate alumina is not expected to increase. In the absence of the aluminum pool, stirring of the electrolyte will be minimized and the current efficiency will remain at around 90%.

An example of a novel approach to cell design is given in the patent of Foster and Jacob (13) in which the TiB_2 is in the form of hollow vertical cylinders embedded in the cathode base. In operation these fill with aluminum and then overflow; very close spacing of electrodes is possible without prejudicing good transport of reactants to the active surfaces. The cylinder electrodes effectively prevent surging of the aluminum and also have the advantage that they require less TiB_2 than the flat tiles.

The practical problems associated with TiB_2 seem to be uneven corrosion and cracking of fabricated parts in the cell environment. It is surprising that given the incentive of 20% improvement in efficiency that the problems associated with producing TiB_2 and its application are not closer to solution.

In view of the major benefit expected to be derived from an extensive retrofit of TiB_2 cathode, every effort should be made to advance this technology by every means possible. It would be useful to have, in the public domain, documentation of the technical and engineering options available in TiB_2 fabrication, and the energy and cost benefits that might be derived from them. These options include the starting materials, method of preparation, slurry casting, cold pressing, sintering, etc.

13.4 Permanent Anodes

Though there are other reasons to consider permanent or non-consumable anodes in the Hall-Heroult cell, such as the elimination of the prebake plant, they will also contribute to reducing the ACD. When permanent anodes are used, the electrode reaction is oxygen evolution rather than the generation of carbon dioxide.

This means that the theoretical open circuit voltage is 2.21V as opposed to the 1.17V for carbon anodes. So the decrease in ACD must more than compensate for this difference if there is to be an improvement in Whr efficiency. The consensus is that an overall improvement of some 8-10% would be achieved if a suitable material were available. The only open literature on this topic is in the form of patents (14) (15) where there are claims for the utility of the following materials:

- Tin oxide, iron oxide, chromium oxide, cobalt oxide, nickel oxide or zinc oxide with small additions of Fe, Sb, Cu, Mr, Nb, Zn, Cr, Co, W, Cd, Zr, Ta, In, Ni, Cu, Ba, or Bi.

- Spinels with the general formula XYY^1O_4 where X is a divalent or tetravelent metal, Y and Y^1 may be the same or different and are trivalent or divalent metals.

- Perovskite oxides with the general formula RMO_3 where R is a monovalent, divalent or trivalent metal and M is a pentavalent, tetravalent or trivalent metal.

It is claimed that certain of these materials are stable in a cryolite melt containing dissolved alumina in an electrolytic cell as long as the cell is under load. There is a requirement for uniform current density and for oxygen to contact all exposed surfaces of the anode.

Large scale tests are reputed to be under way in Europe, and it is generally considered that although major problems have been encountered, the work is continuing. Probably the biggest incentive to develop a permanent anode is the opportunity to design a bipolar cell. It is unlikely that permanent anodes would be considered as a retrofit for existing cells. Progress towards a permanent anode depends on a better understanding of the processes occuring at the anode. Research effort directed at this is strongly recommended.

One other facet of the permanent anode is the opportunity to reduce cell voltage by the use of a depolarizing gas. If, for example, carbon monoxide were fed to the anode, the theoretical open circuit voltage would be lowered to 1.29V. The concept has been demonstrated in bench scale work, but the complexity of a large scale cell and difficulty in maintaining a three phase interface (electrode-gas-electrolyte) probably excludes CO depolarization from practical use. Carbon monoxide could conceivably be used as the depolarizer if the anode were an oxygen anion conductor. The known oxygen ion conductors such as doped zirconia are unstable in cryolite and cannot support very large currents.

Suggestions that hydrogen or methane might be used as depolarizers for a permanent anode are untenable because of extensive hydrogen fluoride production.

13.5 Improved Cell Control

In the course of the last twenty years, the energy consumption associated with the electrolytic reduction of aluminum has fallen from 8-10 kWhr/lb to 6 kWhr/lb for good current technology. This has been achieved by a better understanding of the mechanisms important in cell operation. These include the influence of electrolyte composition, temperature and ACD on cell voltage and current efficiency, and the importance of hydrodynamic effects, and crust shape and thickness. The magnetically induced flow of the aluminum cathode and the electrolyte, with a shear plane at the interface, maintain the elctrolyte saturated with aluminum. The dissolved or suspended aluminum can react with carbon dioxide bubbles swept from the anode to reduce the current efficiency. Crust thickness is a function of temperature and on cooling, it can grow over the surface of the cathode increasing the current density and changing the current distribution in the cell. The change in current distribution alters the magnetic forces and thus the flow pattern. What emerges from this is a complex interaction between most of the major factors that affect cell performance. The result is a fluctuating pattern of continuous changes in cell operation, some over a long period of time, some quite short. A detailed discussion of these effects has recently been presented by Luchi and Arai (16).

In practice, the pattern of behavior of each installation of cells has slowly evolved to the point where high efficiency is routinely obtained, though the patterns are not necessarily the same. Now, with the opportunity for computer monitoring, the control process can be automated and integrated with the feed of alumina, to anticipate the anode effect.

The anode effect occurs when the alumina content of the cryolite electrolyte falls below about 2% by weight. When this happens, the cell voltage increases to between 30 and 40V. Normal operation is restored when alumina is added to the cell, but recovery can take anywhere from five to ten minutes. In older practice, the anode effect was induced several times a day since this imparted stability to the cells and avoided the risk of overfeeding. The latter circumstance, because of the slow dissolution of the alumina in the cryolite results in what is termed a "sick cell", a circumsatnce that might take days to recover. Also, if the alumina sinks through the aluminum to the carbon block manual "demucking" of the cell is needed.

It is now recognized that the anode effect is wasteful of energy and that the time average value for off time constitutes a significant loss. It can be expressed as an effective voltage loss of about 0.1V.

Cell control for optimum operation, including the suppression of the anode effect, can be achieved because of the dynamic characteristics of the cell voltage. When the current and voltage of a cell are monitored, it is found that in addition to the expected dc signal, there is a random fluctuating component that is considered to be due to bubble formation on the anode. Since the number of bubbles controls the contact area between the anode and the electrolyte, there is a natural fluctuation period which is a function of the nominal current. As long as the frequency is within normal bounds, a cell may be said to be in control. An improper frequency can be indicative of low ACD, grounded anode, low aluminum cathode, low electrolyte or an overfed cell.

Control of the anode effect is possible by computing the resistance of a cell from the measured voltage and current and then determining when the resistance begins to increase. At a predetermined increase, the computer demands the addition of alumina to the cell. Methods of monitoring the alumina content of the cryolite have been developed but have not seen use in every day cell operations.

14.0 MISCELLANEOUS PROCESSES FOR ALUMINUM PRODUCTION

14.1 The Toth Process

In this process proposed by Charles Toth (17) manganese metal is used to reduce aluminum chloride to aluminum at 300°C and 15 atmospheres pressure. The reaction may be expressed as

$$3Mn\ (s) + 4Al_cCl_6(l) \rightarrow 3\ (Mn\ Cl_2\ Al_2Cl_6)\ (l) + 2Al(s)$$

The flow diagram for the overall process is shown in Figure 11, the aluminum chloride is obtained by the chlorination of clay with chlorine and silicon tetrachloride at 925°C. The manganese chloride produced in the precipitation of the aluminum powder is separated from the aluminum chloride by allowing the latter to evaporate. The manganese chloride is then oxidized in oxygen at 600°C to produce Mn_2O_3. It is proposed that the oxide in turn be reduced to the metal in a blast furnace for recycle.

It is generally acknowledged that manganese sesquioxide cannot be reduced effectively in a blast furnace and that other methods of metal recovery would not be economic. The magnitude of the problem is apparent when it is realized that three tons of manganese need to be recycled for each ton of aluminum produced. We also consider that the manganese content of the aluminum produced by this method would be unacceptably high.

14.2 Monochloride Process

Peacey and Grimshaw (18) have proposed a process in which aluminum monochloride is produced directly from bauxite at 1800°C. It is subsequently quenched with disproportionation in liquid lead to give liquid aluminum. The aluminum and lead layers separate to give aluminum with less than 1% silicon and just traces of lead. A typical flow sheet is shown in Figure 12. Some steps of the process have been demonstrated in the laboratory but there is no process experience. We estimate that the electrical power requirements for the 1800°C furnace would be comparable to that of the first step of the Gross process at 6.5kWhr/lb. This figure means that the process is scarcely competitive with the Hall-Heroult approach though it might have the advantage of lower capital cost.

14.3 Reduction in Dispersed Arc Discharge

Karlovitz of Combustion and Explosives Research, Inc. in U.S. Patent 4,146,389 issued March 27, 1979 describes the reduction of alumina to aluminum metal in a dispersed electrical discharge with carbon and natural gas.

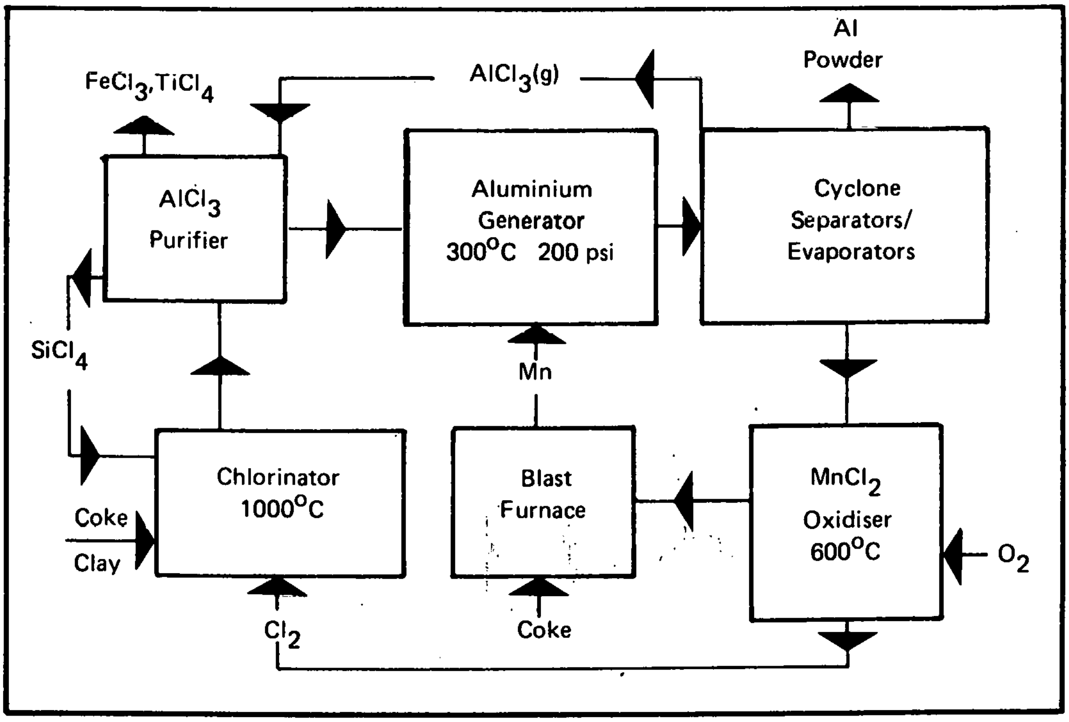


FIGURE 11 TOTH PROCESS FLOWSHEET

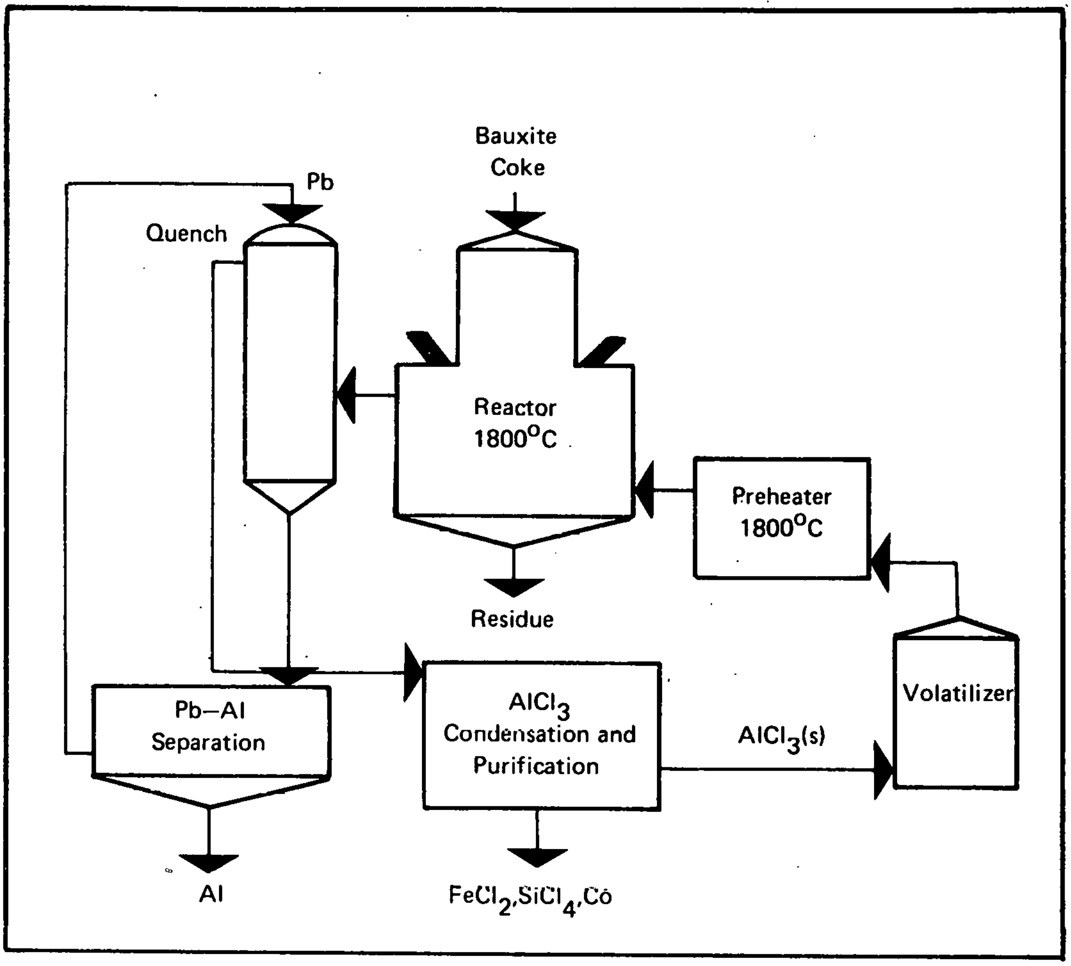


FIGURE 12 MONOCHLORIDE PROCESS FLOWSHEET

$$Al_2O_3 + 3CH_4 \rightarrow 2Al + 3CO + 6H_2$$

The discharge is claimed to operate at low current levels and that if the byproduct hydrogen is taken into account, the patent cites an energy consumption of 4 kWhr/lb, actual electrical energy consumption is 6 kWhr/lb but credit is taken for the hydrogen that is produced. It is acknowledged that the back reaction is significant but that Al_2O_3, Al_4C_3 and Al_2OC are carried through the process as a dust than can be collected and recycled. We believe that these contribute to a low efficiency process and that there is a significant risk that the impurities would condense with the metal.

14.4 Inert Arc Furnace Reduction (Greenwald Associates, Inc.)

Greenwald Associates, Inc. has developed an Inert Arc Furnace in which the furnace atmosphere constitutes the electrical resistance of the system. The furnace is operated closed with a large zone of uniformly high temperature. Thermal losses are said to be minimal. The furnace has been used for making aluminum alloys (low aluminum values <5%) directly from the oxides. The energy consumption for alumina reduction was estimated by Greenwald to be less than 4 kWhr/lb, but no assessment has yet been made of the difficulties associated with separating aluminum vapor and carbon monoxide to prevent the reverse reaction.

14.5 Thermal Dissociation of Halides

It has been suggested U.S. Patent that the halides of aluminum may be dissociated, in a plasma arc, at 4000-5000°C. The concept is thermodynamically sound but it is inconceivable that the products can be quenched fast enough to prevent the reformation of the halide.

14.6 Tripropyl Aluminum Hydride

This process patented by Ethyl Corporation involves the reduction of low grade ores in an electric furnace, with subsequent separation of the aluminum from the aluminum silicon alloy by reaction with propylene and hydrogen to form $(C_3H_7)_3$ Al or $(C_3H_7)_2$ Al. The aluminum is recovered by pyrolysis which also regenerates the propylene. A flow sheet for this process which can be extended to produce ferrosilicon at the same time is shown in Figure 13. It is considered that first step will be similar to the first step of the Gross process and thus quite energy intensive. We also anticipate that the process would be expensive.

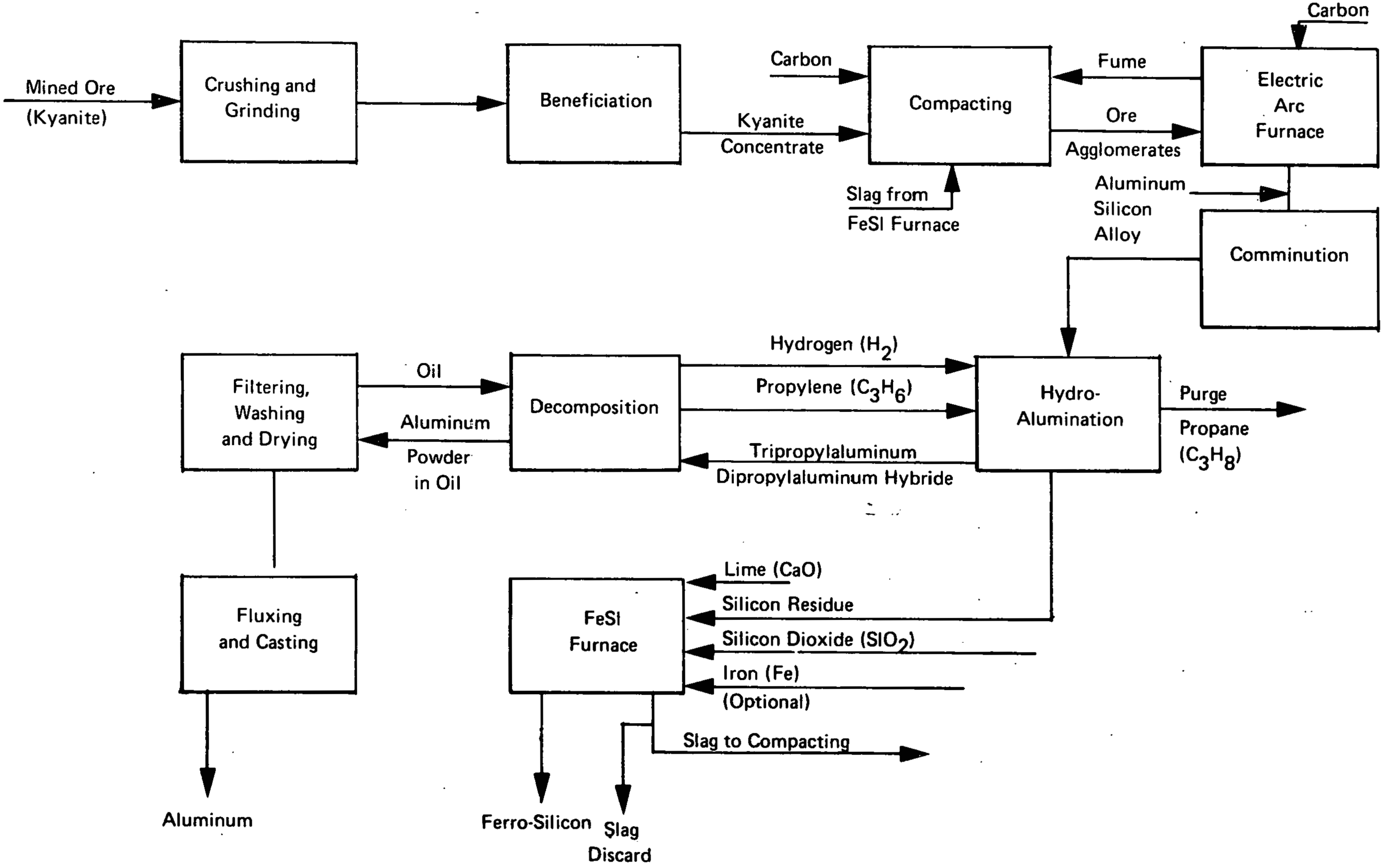


FIGURE 13. TRIPROPYL ALUMINUM PROCESS FLOWSHEET

15.0 RESEARCH AND DEVELOPMENT RECOMMENDATIONS

The near term goals for R&D in the field of primary aluminum are relatively easy to define. These should be to develop cathode materials that will improve the efficiency of the Hall-Heroult cell. Efforts to define a manufacturing process for titanium diboride or the mixed boride-nitride should be stepped up and a more vigorous testing program pursued. The program should probably focus on practical shapes of sufficiently large size for testing under realistic conditions. It is understood that there is already activity in TiB_2 ceramics in Government Laboratories though the work is not directed at cathodes for the aluminum industry. The expertise at these laboratories could form a base for new activities. Other programs should look at the influence of the method of preparation, process variables and composition on performance and life. It is realized that the testing is necessarily a long and involved process, this emphasizes the need for prompt expansion of the testing program. The testing must be backed up with comprehensive characterization of the ceramic components before and after testing.

We also recommend study of materials for a permanent anode, particularly the newer materials developed as MHD electrodes, it would also be worthwhile to examine the thermodynamics of some of the oxide-cryolite systems under the conditions of the very localized, high oxygen partial pressure that can be assumed to occur at the surface of an electrode evolving oxygen.

At a lower level of effort we also recommend ongoing studies of carbothermic reduction, particularly the Al-O-C-Si system. Of interest would be kinetic studies and physical characterization of the melts at high temperatures. These studies might be extended to explore the separation of aluminum-silicon alloys by the subhalide process.

For the longer term the alternative electrolytic processes look as if they could provide some energy savings beyond the possibilities with the Hall-Heroult cell. The chloride process is fully developed and apparently available for licensing so that no research activity is needed in this area. Sulphide electrolysis appears attractive if a) the sulphide can be prepared in high yield without too large an energy penalty and b) the ACD can be kept small without prejudicing current efficiency by the oxidation of soluble monovalent aluminum species that apparently occur to a greater extent in the sulphide system than in chloride and cryolite/alumina systems. Both of these topics deserve close scrutiny.

Nitride electrolysis is faced with the same problem in feedstock preparation and such factors as slow dissolution and low current efficiency at other than very high current densities indicate a complex electrolytic process. However, the system should be studied in detail.

We do not recommend any work on the processes listed in Section 14.

16.0 REFERENCES

1. T.R. Beck, Improvements in Energy Efficiency of Industrial Electrochemical Processes, Final Report on Contract No. ANL/OEPM-77-2, Argonne National Laboratory, January 1977.
2. J.W. Evans, Y. Zundelevich, E.D. Tarapore and D. Sharma, Magnetic Fields, Current-Densities Melt Velocities and Current Efficiencies in Hall-Heroult Cells, Report on DOE Contract No. W-7405-ENG-48, March 1979.
3. L.M. Foster, A. Long and M.S. Hunter, Reactions Between Aluminum Oxide and Carbon, J. Amer. Cor. Soc., 39:1 (1956).
4. P.T. Stroup, Carbothermic Smelting of Aluminum, Trans. Met. Soc. AIME, 230: 356 (1964).
5. V.M. Kozlov, N.S. Guseva and V.N. Veretinskii, Reduction of Alumina by Carbon, Zhurnal Prikladnoi Khimii, 45:1409 (1972).
6. K. Motzfeldt and B. Sandberg, Chemical Investigations Concerning the Carbothermic Reduction of Alumina, Light-Metals, Conf. Proc., New Orleans, 1979, Page 411.
7. K. Motzfeldt and M. Steinmo, Proceedings of the Third Nordic High Temperature Symposium, København, 1973, Vol. 2, page 91.
8. T. Førland, J. Gomez, S.K. Ratkje and T. Østvold, Acta. Chem. Scand., A28:226 (1974).
9. P. Weiss, Method of Producing Aluminum, U.S. Patent 2,843,475 assigned to VAW, July 15, 1958.
10. E.I. Khazanov, A.I. Belyaev, Legkie Metal, 4:1 (1935).
11. A. Bonomi, H. Hadate, F. Breda and C. Gentaz, A Study on Electrolysis of Aluminum Nitride in Molten Salts, Battelle Geneva Research Centre, to be published.
12. E. Peled and E. Gileadi, The Electrodeposition of Aluminum from Aromatic Hydrocarbons, J. Electrochem. Soc., 123:15 (1976).
13. P.A. Foster, S.C. Jacobs, Electrolytic Production of Metal, U.S. Patent 4,071,420 assigned to Alcoa, January 31, 1978.
14. B. Marincek, Electrolytic Process, U.S. Patent 3,692,645, assigned to Swiss Aluminum Ltd., September 19, 1972.
15. K. Yamada, T. Hashimoto and K. Horinuchi, Aluminum Production Method with Electrodes for Aluminum Reduction Cells, U.S. Patent 4,039,401, assigned to Sumitomo Chemical Co., Ltd., August 2, 1977.

16. T. Luchi and K. Arai, Light Metals, 25:267 (1975).

17. C. Toth, Method for the Production of Aluminum, U.S. Patent 3,918, 960, assigned to Applied Aluminum Research Corp., November 11, 1975.

18. J.A. Peacey and W.A. Davenport, Evaluation of Alternative Methods of Aluminum Production, J. Metals, July 1974, page 25.

17.0 BIBLIOGRAPHY

17.1 General (Section 2.0)

The Chemical Background of the Aluminum Industry, T.G. Pearson, Chemical Society, London, 1957.

Environmental Considerations of Selected Energy Conserving Manufacturing Process Options - Alumina/Aluminum Industry Report, R.W. Hyde et al., Final Report on Contract No. EPA-600/7-76-034h, December 1976.

Improvements in Energy Efficiency of Industrial Electrochemical Processes, T.R. Beck, Final Report on Contract No. ANL/OEPM-77-2.

New Extractive Aluminum Techniques, Report of the Light Metals Society and Light Metals Refining Association Committee, Tokyo, 1976.

Some Recent Developments in the Theory of Aluminum Electrowinning, K. Grjotheim, C. Krohn, J. Thonstad, Rev. Pure and Applied Chem., 18, 219, 1968.

Industrial Process Profiles for Environmental Use, Chapter 25, Primary Aluminum Industry Report on Contract No. EPA-600/2-77-023y, February 1977.

From Alumina Powder to Semifinished Product, R.J. Dowsing, Metals and Materials, February 1977, Page 20.

Evaluation of Alternative Methods of Aluminum Production, J.G. Peacey and W.G. Davenport, Journal of Metals, July 1974, Page 25.

Improved Methods and Equipment for Energy Savings in the Aluminum Industry, W.E. Stephens, Light Metal Age, June 1976, Page 5.

Bureau of Mines, Minerals Yearbook, Aluminum, J.W. Stamper and C.M. Monroe, 1977 Preprint.

Aluminum Extractive Metallurgy - Trends, Nolan E. Richards, Proc. Int. Symp. on Electrochemistry, Edited Bloom Plenum, New York 1977 Page 267.

17.2 Carbothermic Processes (Sections 4.0 and 5.0)

Chemical Investigations Concerning the Carbothermic Reduction of Alumina, A. Gitlesen, O. Herstad and K. Motzfeldt.

Reactions Between Aluminum Oxide and Carbon, The $A\ell_2O_3$ - $A\ell_4C_3$ Phase Diagram, L.M. Foster, A. Long and M.S. Hunter, J. Amer. Cer. Soc., 39, 1 (1956).

Carbothermic Smelting of Aluminum, P.T. Stroup, Trans. Met. Soc., AIME, 230, 356 (1964).

Aluminum Carbide Contamination of Molten Aluminum, R.C. Dorward, Aluminum, 49, 686, 1973.

Kinetics of Reactions Between Carbon and Refractory Oxides, K. Motzfeldt and M. Steimmo, Third Nordic High Temperature Symposium, 1972, Page 91.

Reduction of Alumina by Carbon, V.M. Kozlov, N.S. Guseva and V.N. Veretinskii, Translation of Zhurnal Prikladnoi Khimii, 45, 1409 (1972).

Carbothermic Reduction of Alumina, W.L. Worrell, Canadian Metallurgical Quarterly, 4, 87 (1965).

Analysis of the Thermodynamics of the $A\ell$-C-O System in the Temperature Range 1000 - 1800°K, V.C.P. Morfopoulos, Canadian Metallurgical Quarterly, 3, 95 (1964).

Chemical Investigations Concerning Carbothermic Reduction of Alumina, K. Motzfeldt and B. Sandberg, Light Metals.

17.3 Subhalide Process (Section 6.0)

U.S. Patent 3,235,376, Procedure and Apparatus for Subhalide Refining of Aluminum, E.A. Hollingshead and N.W.F. Phillips, February 15, 1966.

U.S. Patent 2,883,162, Condenser with Rotary Scraper, B. Rapson, April 21, 1959.

U.S. Patent 2,914,398, Recovery of Aluminum in Subhalide Distillation, A.H. Johnston and F.W. Southam, November 24, 1959.

U.S. Patent 3,243,282, Recovery of Aluminum from Gaseous Aluminum Monohalide, J.P. McGeer, March 29, 1966.

U.S. Patent 3,274,008, Refractory Compositions and Methods of Preparation, V.A. Braunwarth, A.G. Nickle and N.W.F. Phillips, September 20, 1966.

U.S. Patent 3,311,363, Gas-Liquid Contact Apparatus for Aluminum Refining by the Subhalide Distillation Process, N.W.F. Phillips, B. Rapson, March 28, 1967.

U.S. Patent 3,324,013, Method and Apparatus for Determining Composition of Molten Salt Mixtures, E.W. Dewing, June 6, 1967

U.S. Patent 3,336,731, Procedures for Treating Gaseous Aluminum Halide, N.W.F. Phillips, F.W. Southam, August 22, 1967.

U.S. Patent 3,343,946, Method and Apparatus for Converter Residue Discharge, N.W.F. Phillips, F.W. Southam, September 26, 1967.

U.S. Patent 3,385,695, Procedures and Apparatus for Feeding Particulate Solids into a Condensable Gas, H.J. Howie, May 28, 1968.

U.S. Patent 3,292,914, Preventing Blockage in Apparatus for Mono-Halide Refining of Aluminum, F.W. Southam, December 20, 1966.

U.S. Patent 3,411,759, Apparatus for Splashing Liquids, B. Rapson, November 19, 1968.

U.S. Patent 3,495,813, Gas-Liquid Contact Apparatus, M. Marenghi and B.J. Taylor, February 17, 1970.

U.S. Patent 3,349,160, Apparatus for Passing Electric Current Through Liquids, B. Rapson, October 24, 1967.

U.S. Patent 3,351,461, Procedures for Decomposing Gaseous Aluminum Subhalide, F.W. Southam, November 7, 1967.

17.4 Chloride Electrolysis (Section 9.0)

K. Arjotheim, C. Krohn and H.A. Øye, Aluminum, 51:697 (1975).

H. Linga, K. Motzfeldt and H.A. Øye, Bev. Bunsenges, Phys. Chem., 82:568 (1978).

U.S. Patent 3,786,135, Recovery of Solid Selectively Constituted High Purity Aluminum Chloride from Hot Gaseous Effluent, L.K. King, L.K. Knapp, R.C. Schoener, N. Kloap, B.M. Starner, J.A. Remper, January 15, 1974.

U.S. Patent 3,796,551, Reaction Chamber Construction for the Chlorination of Alumina, R.M. Pope, March 12, 1974.

U.S. Patent 3,811,916, Method for Carbon Impregnation of Alumina, A.S. Russell, N. Jarrett, M.J. Bruno, J.A. Remper, May 21, 1974.

U.S. Patent 3,816,078, Tapering Fluidized Bed Chamber, C.C. Cook and R.M. Pope, June 11, 1974.

U.S. Patent 3,842,163, Production of Aluminum Chloride, A.S. Russell, N. Jarrett, P.T. Stroup, October 15, 1974.

U.S. Patent 3,893,899, Electrolytic Cell for Metal Production, M.B. Dell, W.E. Haupin, A.S. Russell, July 8, 1975.

U.S. Patent 3,847,761, Bath Control, W.E. Haupin, November 12, 1974.

U.S. Patent 3,904,494, Effluent Gas Recycling and Recovery in Electrolytic Cells for Production of Aluminum from Aluminum Chloride, S.C. Jacobs and R.C. Schoener, September 9, 1975.

U.S. Patent 3,929,975, Selective Recycle Production of Aluminum Chloride, L.K. King and N. Jarrett, December 30, 1975.

U.S. Patent 3,930,800, Fluidized Bed Desubliming Apparatus for Recovery of Aluminum Chloride, R.C. Schoener, L.K. King, L.L. Knapp, N. Kloap, January 6, 1976.

U.S. Patent 3,956,455, Recovery of Solid Selectively Constituted High Purity Aluminum Chloride from Hot Gaseous Effluent, L.K. King, L.L. Knapp, R.C. Schoener, N. Kloap, B.M. Starner, J.A. Remper, May 11, 1976.

U.S. Patent 3,959,439, Aluminum Chloride Production Process, R.M. Pope, May 25, 1976.

U.S. Patent 4,039,647, Production of Aluminum Chloride, D.A. Wohleber, C.N. Cochran, August 2, 1977.

U.S. Patent 4,133,727, Method for Extracting Heat from a Chamber Containing a Molten Salt, E.H. Rogers, Jr., January 9, 1979.

U.S. Patent 4,108,741 Process for the Production of Aluminum, Y. Tsumura August 22, 1978 assigned to Mitsui

U.S. Patent 4,159,928 Process for the Production of Aluminum, Y. Tsumura July 3, 1979 assigned to Mitsui.

17.5 Hall-Heroult Process (Section 13.1)

Aluminum Electrolysis - The Chemistry of the Hall Heroult Process, K. Grojotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, J. Thonstad, Aluminum - Verlag GM6H, Dusseldorf 1977.

A Hundred Years of Aluminum Electrolysis, C. Crussard, Trans. Inst. Mining and Metallurgy 87, C147 1978.

See also General Bibliography.

17.6 Titanium Diboride Cathodes (Section 13.3)

Robert A. Lewis U.S. Patent 3151053 - Metallurgy Sept. 29, 1964 assigned to Kaiser Aluminum and Chemical Corp.

Curtis J. McMinn U.S. Patent 3274093 Cathode Construction for Aluminum Production, Sept. 20, 1966 assigned to Reynolds Metals Co.

John L. Dewey U.S. Patent 3 093 570 Refractory Lining for Aluminum Reduction Cells June 11, 1963 assigned to Reynolds Metals Co.

Charles E. Ransley U.S. Patent 3 215 615 Current Conducting Elements for Aluminum Production Cells Nov. 2, 1965 assigned to British Aluminun Co. Limited.

Nolan E. Richards et al U.S. Patent 3 328 280 Cathode Current Collectors, June 27, 1967 assigned to Reynolds Metals Co.

Robin D. Holliday U.S. Patent 3,661,736 Refractory Hard Metal Composite Cathodes for Aluminum Reduction Cell, May 9, 1972 assigned to Olin Mathiesan Chemical Corporation.

Roger A. Steiger et al British Patent 1,526, 443, Refractory Metal Boride Powder, 1978 assigned to PPG Industrict.

Maurice Alliot et al U.S. Patent 3,961,995 Mother Alloy of Aluminum, Titanium and Boran and Process for Fabrication June 8, 1976 assigned to Pechiney.

Warren Goodnow et al Energy Savings Through the Use of an Improved Aluminum Reduction Cell Cathode Reports on ERDA Contract No E (04-3)-1257, Kaiser Aluminum and Chemical Corporation.

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