7. ALTERNATIVE PROCESSES

The Hall-Héroult process has produced essentially all the commercially available aluminum ever used. After more than 125 years the process remains fundamentally unchanged and unchallenged as the only commercially viable way to produce the metal. However, there are a number of deficiencies with the process, namely:

- The energy efficiency is only around 50%.
- It produces twice as much carbon dioxide as aluminum.
- It produces on occasion some of the most powerful greenhouse gasses known (e.g., perfluorinated carbons).
- It has a number of health and safety hazards (high temperature, molten materials, electrical potential, mobile equipment, gaseous and dust emissions) and the requirement for significant manual intervention.
- There is potential for high levels of damaging fluoride emissions.
- The primary metal production cost is more than its chief rival (steel) which restricts its use in a number of applications for which it would be ideal (e.g., transportation).

These deficiencies are well known and documented and have been the driving force to develop alternative processes, although none of them have succeeded. The papers in this relatively short section are some of the better documented attempts to replace the Hall-Héroult process. A lot of research effort has been applied to the, as yet unsuccessful, development of inert anode and drained cathode technologies. These topics are covered in *Electrode Technology for Aluminum Production* (Volume 4 of this *Essential Readings in Light Metals* collection).

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IMPACT OF ALTERNATIVE PROCESSES FOR ALUMINIUM PRODUCTION

ON ENERGY REQUIREMENTS

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SUMMARY

Increasing prices and shortage of large blocks of electrical energy have added further impetus to the search for viable alternative processes. These include electrolysis of aluminium chloride, sulphide, and nitride, carbothermal reduction of either the ore or alumina, and disproportioning reactions of either aluminium sulphide or by the monochloride route. Common to all of these processes, the starting material is an ore containing aluminium oxide and the final product the metal. Thus the thermodynamic cycle will invariably dictate similar theoretical energy requirement.

In practice, however, the achievable efficiencies for the various stages of operation can vary, and more noticeably the proportion of electrical to carbothermal energy required.

The present status indicates that while alternative routes - such as the Alcoa-AlCl₃-Smelting Process, show distinct potential for reducing the electrical energy requirements, they offer little chance of reduction in the overall energy requirements. Furthermore the gains may be made at the expense of production costs because of more stringent purity requirements. From *Light Metals 1981*, Gordon M. Bell, Editor

INTRODUCTION

The aluminium industry is experiencing a major shift in emphasis with it no longer being selective in the development sites based on electricity pricing. Now the limited availability of electricity for expansion has made essential that the future generation of aluminium smelters optimize their energy efficiency. This change has also influenced the emphasis being placed on alternative process technology. Formerly the minimizing production cost was aimed at, but now processes must also be considered with having regard to their implications on both total and electrical energy consumptions. The added costs that conventional aluminium smelters have been faced with in conforming with environmental legislation favour alternative processing technology. However, environmental concern is also retarding the rate of development of new approaches since they must simultaneously assess their environmental impact.

Because of the chemical stability of all aluminium containing ore bodies, large amounts of energy will be required irrespective of the process used. In practice there are only two forms of energy that can be considered, these being carbon (derived from non-renewable coal) and electrical energy (based on the renewable hydropower, the abundant nuclear fuels, or coal). Liquid hydrocarbons have priced themselves out of consideration except in rare instances where their chemical structure can be used to facilitate a specific process stage. In the short term future, electrical energy consumption needs to be assessed in terms of a fossil fuel equivalent for its generation as much of the expansion in generating capacity is based on coal-fired thermal generators. When coal is used, it is assumed that the electrical power is generated with a 33% efficiency. However, in the long term, when nuclear power generation assumes universal acceptability, this consideration may again need to be changed because of the delicate balance that can exist between the supplies of the various energy sources.

ALTERNATIVE PROCESSING AND ENERGY

A diverse range of process variations has been conceived, both because of the different minerals that can be used as raw-material, and the various intermediates that can be formed in the route towards the pure metal. Different reductants have also been proposed.

Figure 1 presents a simplified general flow sheet to represent this range of processes. As will be seen in subsequent discussion this flow sheet only requires minor variations to conform with the actual one for each of the processes being promoted as a likely alternative extraction path. This flow sheet is a sobering reminder that there can be no revolutionary energy saving path to the metal:

All process options start with similar materials, use the same reductant (carbon, either directly or indirectly), produce the same product (aluminium) and similar by-products (oxides of carbon). Overall reaction energy requirements are dependent on these factors only and are independent of path, consistent with the laws of thermodynamics. However, by changing reaction paths, it is possible to vary the ratio of electrical to thermal energy. Also, in practice, savings can be made in energy by having process steps that can be performed with higher relative efficiencies.

<u>Thermodynamic Requirements</u>: Because of the endothermic nature of the reaction to produce the metal from alumina, the enthalpy (ΔH°) of the reaction represents the minimum or theoretical energy required, without differentiating between electrical and thermal components. The formation of intermediates

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Figure 1. General flow sheet for production of aluminium.



Figure 2. Thermodynamic cycle for reduction of alumina.

From Light Metals 1981, Gordon M. Bell, Editor (such as an alloy, AlCl₃ or Al₂S₃) theoretically does not influence the energy requirements, but rather is done for ease of process stages. The thermodynamic cycle commonly used for the Hall-Héroult cell [1] has been modified to encompass the wider range of conditions used in the alternative processes and this is presented in Figure 2. This allows for varying proportions of CO2 and CO in the gaseous product as well as different temperatures for formation and release of gas. The overall enthalpy requirement per tonne of aluminium produced would be given by the expression

$$\Delta H_{\text{TOTAL}}^{O} = \frac{10^{\circ}}{27} \left[\Delta H_{\text{T}}^{\circ} + \frac{1}{2} (H_{\text{T}}^{\circ} - H_{298}^{\circ})_{\text{Al}_{2}\text{O}_{3}} + \frac{3}{4} z (H_{\text{T}}^{\circ} - H_{298}^{\circ})_{\text{C}} + \frac{3(2-z)}{4} (H_{\text{T}}^{\circ}, - H_{\text{T}}^{\circ})_{\text{CO}_{2}} + \frac{3(z-1)}{2} (H_{\text{T}}^{\circ}, - H_{\text{T}}^{\circ})_{\text{CO}} \right]$$
(1)

where

 ${}^{\widetilde{\Delta}H}^{O}_{T}$ is the enthalpy of the reaction at T K, T is the reaction temperature,

T' the exit gas temperature, and $(H_T^0)_i$ is the enthalpy content of component i.

In equation (1), z is the carbon stoichiometric factor according to the overall equation

$$\frac{1}{2}A1_{2}O_{3} + \frac{3}{4}zC = A1 + \frac{3(2-z)}{4}CO_{2} + \frac{3}{2}(z-1)CO$$
(2)

Using this relationship and reliable thermodynamic data [2] energy requirements have been calculated for a range of conditions as summarized in Table I.

Table I. Thermodynamic Energy Requirements for Reduction of Alumina with Carbon under Various Process Conditions.

Reaction	Compositi	on of gas	Exit gas	Energy
temp. K	%CO2	%CO	temp. K	GJ/tonne
1000	100	0	100 0	22.16
	100	0	500	21.46
1000	50	50	1000	24.69
	50	50	500	23.90
1000	0	100	1000	27.23
	0	100	500	26.35
1500	100	0	1500	23.49
	100	0	500	22.00
	50	50	1500	26.11
	50	50	500	24.45
	0	100	1500	28.72
	0	100	500	26.89
2000	100 100 50 50 0 0	0 50 50 100 100	2000 500 2000 500 2000 500	24.86 22.55 27.56 25.00 30.26 27.46
2500	$ \begin{array}{r} 100 \\ 100 \\ 50 \\ 50 \\ 0 \\ 0 \end{array} $	0 50 50 100	2500 500 2500 500 2500 500	26.33 23.09 29.03 25.54 31.82 27.98

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This table demonstrates that for minimum reaction energy requirements it is desirable to operate at as low a temperature as possible and to have as high a proportion of CO_2 as can be achieved. It should be noted, however, that for the production of CO_2 at temperatures above 1000 K an electrochemical mechanism is required since, energetically, CO is the favoured reaction product.

Mineralogical Form of Ore: Aluminium is the third most abundant element and occurs in a wide range of mineralogical deposits. Although bauxite has the highest aluminium content, processes have been proposed for some other sources. The different processes have sometimes been motivated by the desire to use a local or strategic supply and on other occasions for convenience of process path. Because of the structural simularities of many of these ores, the choice of raw-material here would not be expected to have a significant impact on energy requirements. This has been demonstrated in a recent report [3] where different processes were evaluated for the extraction of alumina from three different starting materials. Table II summarizes these options and compares the estimated net energy requirements. Except when the starting

Table II. Energy Estimates for Production of One Ton Alpha Alumina by Various Paths.

Raw material	Formula	A1203 wt%	Extraction process	Process energy GJ/tonne
Alunite	$K_2SO_4 \cdot A1_2(SO_4)_3 \cdot 2A1_2O_3 \cdot 6H_2O_3$	12	Reduction Rost-Bayer	27
Anorthosite	x•NaAlSi ₃ 0 ₈ ,yCaAl ₂ Si ₂ O ₈	26%	Lime-sinter	65
Kaolinite	A1 ₂ 0 ₃ ,2SiO ₂ ·2H ₂ O	36%	 HNO₃ ext HCl ext.evap. crystallization HCl ext.HCl in- duced cryst. H2SO₃ ext. 	39 33 25 29
Bauxite	Al ₂ O ₃ •xH ₂ O,Fe ₂ O ₃ ,SiO ₂	55	NaOH-Bayer	29

material is in an extremely stable form (e.g. anorthosite), the energy requirements are similar to those required for the extraction of alumina from bauxite via the conventional Bayer process. Therefore, although the subsequent discussions concentrate on processes involving either pure alumina or bauxite as the starting material, the energy implications will be more general.

Electrochemical Processes and Energy Efficiencies: Although electrochemistry provides an attractive path for providing the Gibbs energy required in endothermic reactions, in practice the energy efficiency is always less than theoretical. One reason for this is that the reactions are seldom selectively quantitative according to Faraday's Law. The second, and more important reaso is that the voltage for any electrometallurgical process exceeds that theoretically predicted because of ohmic and polarization losses. The cell voltage applied, V_A , can be represented by the equation

$$V_{A} = E_{rev} + \eta_{A} + \eta_{C} + V(R_{i}, R_{e})$$
(3)

where

- ${\rm E}_{{\rm rev}}$ is the reversible thermodynamic potential of the overall cell reaction
- n_A and n_C are the anodic and cathodic overvoltages, and
- V(R_i,R_e) denotes ohmic contributions due to ionic resistance
 - (R_i) and electronic resistance (R_e) .

The electrode polarization and ohmic voltage drops are manifested as heat,

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and for a given cell design the magnitude of the rate of heat generation must be adjusted to maintain a thermal balance. Thus while the objective is to reduce polarization and ohmic voltage drops, voltage reduction must be accompanied by a current density increase or alternatively supplementary heating. This restriction has been a major encumbrance in attempts to lower cell voltage in the Hall-Héroult process even through the anode polarization is high at about 0.5 volts [4] and the ohmic voltage drop exceeds 2 volts.

The electrode polarizations, $n_{\rm A}$ and $n_{\rm C}$, increase with current density but in practical processes they are limited to less than 0.7 volts to avoid concentration polarization. Polarization can be varied a limited amount only by optimizing the electrolyte composition; but otherwise reduction in anodic polarization can be achieved by changing reaction mechanism with appropriate variations in electrode material. Unfortunately, though, for aluminium extraction the range of electrode materials is restricted by the temperatures necessary and the corrosive nature of the electrolytes. Practically therefore it is desirable to reduce the current density to lower the polarization.

Ohmic voltage losses are closely related to cell design and invariably increase as the number of joints between construction materials is increased. Where gas evolution occurs, the electrode design can play an important role in channelling the gas away from the inter-electrode spacing and thus lower the resistance, but such a change can only be effected with non consumable anodes. Generally, ohmic voltage losses can be reduced by reducing interelectrode spacings, and minimizing lengths of electronic conductors. Based on energy and production considerations, an ideal electrolytic cell should satisfy the following criteria whenever feasible:

- cell voltage should be close to theoretical
- the electrodes should maintain dimensional stability
- electrode design should minimize losses in current efficiency
- the cell should maximize electrode area in a given cell volume
- release of evolved gases and removal of deposited metal should be simple
- circulation of the electrolyte should be adequate for maintaining uniform concentration of electroactive species.

For reasons alluded to above, practical cells usually fall a long way short of the ideal. For example, in the chlor-alkali industry, the diaphragm cells operate with only about 53% energy efficiency while the efficiency of mercury cells is about 70%. Therefore, because of the higher temperatures involved, it is not surprising that the existing Hall-Héroult cells operate with an efficiency around 40%, a little lower than magnesium cells.

As will be discussed below, some of the ideal criteria listed above can be incorporated into bipolar cell designs when a large number of electrode pairs are used, thus improving efficiency.

Thermal Processes and Energy Efficiencies: In these processes, where the enthalpy of reaction is generated by combustion, inefficiencies can be the result of a number of causes. These include:

- reactions not being quantitative
- the need to heat impurities or inert materials associated with reactants
- heat transfer from the reactor
- the inability to achieve perfect heat transfer between the heating media and reacting system

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- design restrictions preventing efficient waste heat recovery.

Oxygen enrichment has been used to improve the efficiency of the basic combustion processes by minimizing the enthalpy content of the inert nitrogen, but despite this, the enthalpy content of heating gases causes a marked reduction in energy efficiency for processes requiring temperatures about 2000 K and above. Indeed supplementary electrothermal heating then may be necessary. Reaction efficiency is strongly dependent on the separation of phases, and this in turn is related to the volatility of the metal. In blast furnaces used for iron making the presence of a slag, plus the effective separation of metal and gas leads to fairly efficient reaction. The energy efficiency is also aided by the fast kinetics of the process and efficient preheat of the reacting charge by the gases evolved thus leading to minimal losses.

In practice, the adverse effects of volatilization of metal can be reduced by alloying and this also serves to lower the reaction temperature. However, it is then necessary to have a subsequent metal refining stage.

Generally, the biggest problem in energy efficiency is the recovery of heat from byproducts. This invariably becomes worse as the number of process stages increases because of the difficulty in effecting heat transfer.

For thermal reduction of aluminous ores, high temperatures are necessary because of these ores extreme chemical stability. At these temperatures (in excess of 2000 K) the thermal efficiencies of fuels deteriorate to the extent that it may be necessary to use electrical heating. Furthermore the formation of volatile sub-valent species and the relative high vapor pressure of aluminium will mitigate the energy efficiency being high.

THE ALTERNATIVE PROCESSES

A recent review by A.D. Little Inc. [5] has evaluated the various process options. The more viable options are all based on the overall reaction given by equation (2). They differ in the intermediates formed (e.g. AlCl₃, Al₂S₃, Al₄O₄C and Al-Si alloy), the maximum temperatures achieved, and the method by which electrical energy is used to supplement the overall energy requirement.

Routes Involving Aluminium Chloride

Alumina can be chlorinated in the presence of a reductant, such as carbon, according to the equation

$$Al_2O_3 + \frac{3}{2}zC + 3Cl_2 \rightarrow 2AlCl_3 + \frac{3}{2}(2-z)CO_2 + 3(z-1)CO$$
 (4)

in the temperature range 900-1200 K. Other reductants can also be used (e.g. CO) with a limited variation in the temperature necessary. Metal can be produced from the $AlCl_3$ by electrolysis in a molten salt bath. This approach has been known for more than a century, and was subjected to intensive investigations by Alusuisse in the period around World War I before being abandoned because of technical and economic difficulties. Included among these problems was the tendency for the chloride to hydrolyse and form oxychloride sludges. Interest was revitalized with announcement of the Alcoa Smelting Process [6] and subsequently other variations in the overall process have been considered.

The Alcoa Smelting Process (ASP): The two major innovations covered in their patents are the production of high purity aluminium chloride, and the design of an energy efficient cell for the electrolyses.

The initial stage of the process is to refine the bauxite to alumina via the Bayer process, taking care to control the physical form (such as surface

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area, crystal structure *etc.*) for optimum conditions in the chlorination according to equation (4). The alumina is then impregnated with carbon by thermal decomposition of fuel oil in a fluidized bed system at about 1150 K. Chlorination is carried out in the presence of a catalyst in a reactor heated to between 900 K and 1100 K. These conditions ensure that the gas evolved is predominantly CO_2 , thus minimizing total energy requirements (refer Table I). Although the chlorination reaction is exothermic, the production of aluminium chloride from alumina has been estimated to require approximately 20 GJ/tonne of aluminium content. To this must be added another 45 GJ/tomme for the mining operation and Bayer extraction process.

Aluminium is generated from the chloride by electrolysis in a molten chloride system at about 1000 K and the chlorine is liberated for recycling. The decomposition voltage for this reaction is approximately 1.85 V which is significantly higher than the 1.2 V for the Hall-Héroult process. In the older methods for electrolyzing aluminium chloride containing melts, the voltage was much higher than the theoretical value because of the large interpolar distance. However, in the ASP process the voltage can be maintained much lower than that required for the conventional processes because of the improved cell design that has been achieved. This cell, which is schematically illustrated in Figure 3, combines many of the desirable features discussed above. It has been possible to incorporate these through the use of a less corrosive electrolyte and inert electrodes.

A carbonaceous material has been developed that is suitable for a bipolar arrangement. This material can be fabricated to be given a geometrical form to the electrodes which enables the anode gas to be effectively channelled from the inter-electrode spacing. Small inter-electrode spacings are possible, because of this and the absence of a turbulent metal pad, thus reducing this ohmic voltage loss. A greater gain, when compared to the Hall-Héroult cell, is made by reducing the electronic resistance to that of the thickness of the bipolar electrodes. However, heat balance can still be maintained because of the lower operating temperature and the large number of electrode pairs that





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can be fitted into a given cell volume. While accurate details of operating conditions have not been released, it is obvious that the cell voltage and electrical energy requirements are much less than in the Hall-Héroult process. Table III compares a breakdown of the estimated cell voltage with that for the Hall-Héroult cell when both are operating at about 90% current efficiency. It should be noted, however, that also some current efficiency loss is inevitable when bipolar cell designs are used because of current leakage.

Table III.	Voltage	and Energy	Comparison for	ASP	and	Ha11-
	Héroult	Single Cell	l Equivalent.			

Parameter	Hall-Héroult	ASP cell (estimated)
Decomposition voltage	1.18	1.85
Electrode polarizations $(\eta_A + \eta_C)$	0.50	0.40
Ionic (electrolyte) resistance drop	1.60	0.55
Electronic (electrode) resistance drop	1.02	0.20
Total cell voltage	4.3	2.9
Assumed current efficiency	90%	90%
DC kWh/kg	14.2	9.6
(GJ/tonne)	(52)	(35)
Equiv. GJ required/tonne	155	104

Estimates of the type presented in Table III can be erroneous while the practical cell performance may also fall short of expectations. Clearly though, provided the cell can ratain its dimensional stability and design criteria, the electrical energy requirements can be kept much lower than for the existing process. The proviso relies heavily on the aluminium chloride purity being maintained at the high level (e.g. water and oxide free).

The total energy for the process has been estimated to be between 135 and 170 GJ/tonne aluminium which is still a considerable saving compared to the existing process.

Bauxite Chlorination Route (BCR): Gardner and Milne [7] have evaluated routes for producing the required grade of $AlCl_3$ directly from bauxite, thus by-passing the energy inefficient Bayer process. Their proposal is then to incorporate this with the reduction stage of the ASP. The key to their process is to use carbon monoxide as the reductant as this can be produced from inexpensive coals via, for example, the Cosorb Process [8]. Milne [9] has shown that the chlorination kinetics are favourable at about 900 K. Complications associated with iron chlorides can be overcome by incorporating a preliminary benefication stage. However, a distillation procedure is necessary for separating a pure AlCl₃ from the other chlorinated products.

Estimates of the BCR-process compared to the chlorination process in equation (4) show that there may be a slight reduction in energy in the BCR-route, but the difference would be small.

The total requirement to produce $AlCl_3$ is estimated to be about 70 GJ/tonne of metal produced while reduction requires an electrical energy of about 35 GJ/tonne of aluminium. While this process has not been demonstrated on an integrate pilot scale, it offers a viable optional route for the more difficult stage of the ASP process.

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to produce other, water- and oxide-free, $AlCl_3$ -complexes which can be used as direct addition to the new Alcoa cell. Of course, presently, their energy requirements is very uncertain.

Metal Reduction of AlCl₃: There are few metals capable of displacing aluminium according to the reaction,

$$xM + A1Cl_3 \rightarrow M_{y}Cl_3 + A1$$
 (5)

For practical application such a reaction must be quantitative and the phases of reactants and products should be different to enable physical separation. Metals (such as sodium) that satisfy these requirements are invariably more energy intensive to produce.

Toth [10] proposed using manganese as the reductant, but this would have had problems because the metals both come out in the solid phase. Furthermore, the reduction of manganese oxide could not be carried out without use of electrical energy. Although conceived as a process to eliminate electrical energy, it would have a higher electrical energy demand (about 100 GJ/tonne of direct electrical energy) and the highest total energy demand (about 300 GJ/tonne) of all processes conceived.

Routes Involving Aluminium Nitride

Formation of aluminium nitride according to the reaction

$$A1_2O_3 + 3C + N_2 = 2A1N + 3CO$$
(6)

becomes favoured at about 2000 K and this has been considered a potential intermediate for production of the metal [5]. The metal can be produced by either thermal decomposition of the nitride at temperatures of about 2700 K, or by electrolytic decomposition in a suitable solvent.

Hitherto, however, efficient production of the nitride has not been demonstrated, and the process is probably complicated by the formation of suboxides, aluminium carbide, aluminium oxy-carbide and cyanides. Thus it is likely to be an inefficient and energy-intensive reaction. Compared with the simple and more favourable chlorination reaction, it is reasonable to suggest that the production of aluminium nitride would require at least 100 GJ/tonne of aluminium.

Electrolysis of AlN: If, however, an efficient method can be devised for the production of AlN, this could provide an exciting alternative. The decomposition voltage for the reaction

$$2A1N = 2A1 + N_2 \tag{7}$$

would be 0.72 V at 1000 K, while the evolution of N_2 would ensure the anode was not consumed. Thus efficient cell designs like that proposed for the ASP would be possible. The electrochemical energy requirement would be about 25 GJ/tonne metal. However, finding a suitable solvent would present a challenge.

Thus while the process can not be considered viable now, it represents a "long-shot" for low electrical energy in the future.

Thermal Decomposition of AlN: Because of the high reaction temperature, and the difficulty in separating the two gaseous products, this would be more energy intensive than the electrolytic route.

Other Routes: In the relative near future it may be possible economically

The temperatures necessary for formation of aluminium sulphide by the reaction

$$A1_2O_3 + \frac{3}{2}S_2 + 3C \rightarrow A1_2S_3 + 3CO$$
 (8)

fall between those necessary for chlorination and AlN formation. Although there are no reliable data, the reaction temperature will probably have to exceed 1400 K to ensure the sulphide melts for phase separation. Energy requirements would exceed that for the chloride formation and therefore be in the range 80-100 GJ/tonne. However, as kinetic data for formation of the sulphide is limited, this figure could prove to be conservative.

<u>Electrolysis of Al_2S_3 </u>: Production of metal from the sulphide would be carried out electrolytically at a decomposition voltage of about 1.2 V. Cell design would again be efficient since carbon electrodes would remain dimensionally stable.

Experience in electrolysing other sulphide solutions, [11] and [12], would suggest, however, that current efficiencies will be low. Sulphur has a tendency to dissolve in electrolytes containing sulphide ions, [12] and [13], forming subsulphides. These can be reduced at the cathode. Thus current efficiencies in bipolar cell systems may even be below 70%. Electrical energy requirements would therefore be similar to the amount used in AlCl₃ electrolysis (e.g. about 35 GJ/tonne). The viability of this option would revolve around the relative ease for production of Al_2S_3 as compared to AlCl₃ and environmental problems.

Carbothermal Reduction Paths

Direct reduction of alumina takes place according to the over-all reaction

$$A1_2O_3 + 3C = 2A1 + 3CO , (9)$$

Process temperatures in excess of 2300 K are required. The theoretical energy requirement (cf. Table I) is approximately 50% higher than the theoretical value for production of metal via the Bayer/Hall-Héroult path. On the other hand, the energy efficiency of, e.g., an industrial submerged-arc electric furnace is considerably better than that of a Hall-Héroult cell, so that the two processes might break even with respect to energy requirement, if other obstacles to the carbothermic reduction could be overcome.

Carbothermic Reduction of Alumina: The over-all reaction (9) in practice takes place in several steps. In the first step, the tetroxy-carbide is formed:

$$2A1_2O_3 + 3C = A1_4O_4C + 2CO$$
(10)

and then the carbide

$$A1_{4}O_{4}C + 6C = A1_{4}C_{3} + 4C0$$
(11)

In the final step, metal is formed by reaction between oxycarbide and carbide:

$$A1_{4}O_{4}C + A1_{4}C_{3} = 8A1 + 4C0$$
(12)

The metal-producing step, however, requires temperatures around 2400 K, at which temperatures the oxycarbide and the carbide are present as a mixed oxide-carbide melt, thus equation (12) should be regarded as only schematical.

At the process temperature, the reaction gas will contain considerable

amounts of Al and Al₂O vapors which may result in metal loss. Even more serious is the fact that the liquid metal at the reaction temperature will contain dissolved carbon in the amount of about 20 atom. On cooling of the metal, this carbon precipitates as Al_4C_3 , rendering about one-third of the metal value unavailable, and at the same time necessitating a final separation or purification process.

Direct carbothermic reduction of alumina has never been developed to a commercial process. It is thus difficult to give figures for the actual energy requirement, but it is estimated that it could be as high as twice that for the present electrolytic process [14].

Reduction of Clay or Alumino-Silicates: Reduction of alumina in its mixtures with other oxides to form an alloy is thermodynamically more favourable and thus requires lower process temperatures. During World War II some plants using this process were in operation in Germany.

Reduction to an aluminium-silicon alloy, which again has attracted particular interest, has been described by the following steps [15]:

$$3SiO_2 + 9C = 3SiC + 6CO$$
 (13)

$$2A1_2O_3 + 3C = A1_4O_4C + 2CO$$
(10)

 $A1_40_4C + 3SiC = 4A1 + 3Si + 4C0$ (14)

In addition to lowered reaction temperature, the process also has an advantage in that the solubility of carbon in the metal is lowered in the presence of silicon.

Aluminium-silicon alloys may be produced by this route with heat generated by the combustion of carbon. The thermal efficiency in this case is very much dependent on the feasibility of pre-heating the oxygen (and eventually the carbon) to the highest possible temperature. In any case the process, in addition to the alloy, will produce large quantities of carbon monoxide. Hence it would seem energetically and economically attractive only in the cases where a need exist for these quantities of carbon monoxide (for heating purposes or chemical syntheses) on the same plant site. Because this process avoids electrical energy completely, its energy requirements are much lower than the other options considered. Estimates are in the range 75 to 100 GJ/tonne.

A limited market exists for aluminium-silicon alloys. For the production of commercially pure aluminium via this route, a final purification step would be required, with increased energy requirement as a consequence.

COMPARISON OF ENERGY REQUIREMENTS

The basis of comparison is inevitably the existing overall process which is the combined Bayer/Hall-Hároult processes (B/H-H). The energy requirements for this has undergone a steady reduction. Smelters employing the best technology now require less than 13 kWh/kg of metal produced, which is equivalent to 47 GJ/tonne of metal. Various predictions have been made on the reductions that may be achieved by design modifications, but it is unlikely that it can be reduced below 11 kWh/kg without the introduction of dimensionally stable anodes. The inherent features of the design for a consumable anode and the need to maintain a heat balance would mitigate any greater reduction. Thus, we choose to use the more realistically achievable value as the basis for comparison.

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To the energy above we must add the thermal energy requirements. When the energies of the Bayer process, the mining and ore benefication, the carbon anodes and their preparation, are taken into account, we have an additional thermal energy requirement of about 80 GJ/tonne. Thus, the net energy requirement would be about 127 GJ/tonne.

As outlined in the introduction, current practice is to assume the electrical energy is generated by combustion of a fuel. Since this conversion is only about 33% efficient, we need to add the indirect electrical energy loss to obtain the gross energy. For example, this would add another 94 GJ/tonne to the Bayer/Hall-Héroult route requirements.

Figure 4 compares graphically the energy estimates for the various processes considered. It must be emphasised that the reliability of the estimates made is limited because of lack of data. However, the comparison is still useful in demonstrating that all the processes are energy intensive. The better routes generally have lower maximum process temperatures, as exemplified by the chlorination-chloride electrolysis routes.



Figure 4. Estimated energy requirements for various processes.

It should be noted that thermal reduction of clays to form an aluminium silicon alloy has not been included in the comparison. Without refining it would only satisfy a limited market. Refining of such an alloy would be energy-intensive and it is then unlikely that the net energy requirements would be lower than the more promosing chloride routes.

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