

ALTERNATE SMELTING PROCESSES FOR ALUMINUM

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Alternate aluminum smelting processes are considered for meeting the cost challenge of the cyclical aluminum ingot market and increasing the competitiveness of aluminum in material markets. Experience with 46 metals shows average abundance in the earth's crust and extractive technology are the main determinants of price. Metals produced by thermal methods have the lowest market price. Those produced electrolytically are many times higher. Nearly every cost sector of the Bayer/Hall-Heroult process must be addressed for a major cost reduction in aluminum. This may include improving energy efficiency and productivity (labor and capital), changing to less expensive energy forms, combining purification and reduction to use less expensive raw materials and reductants and producing valuable by-products. Bipolar cells using alumina may offer productivity and energy improvements without costly chemical conversion of alumina. Carbothermal processes can reduce nearly every cost sector if better ways can be found to suppress vaporization and side reactions and facilitate removal of aluminum from the products.

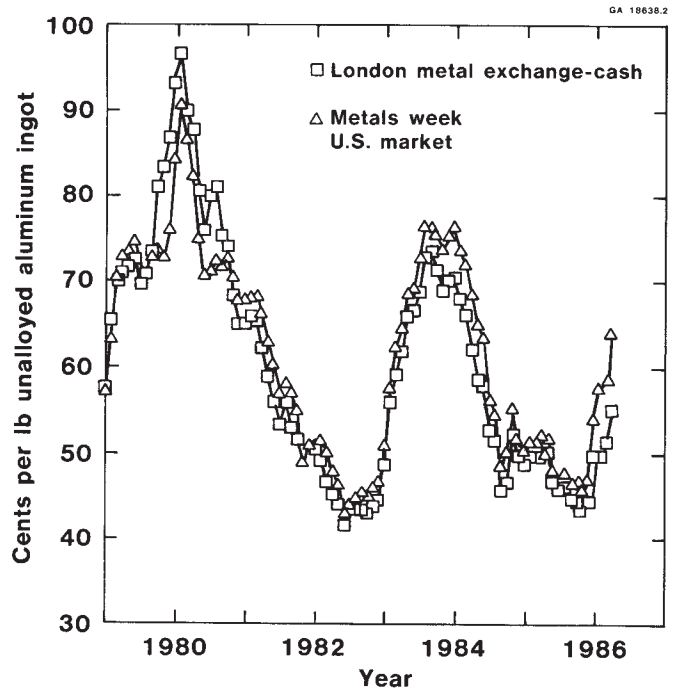
Introduction

Intense competition within the world aluminum industry and increasing market rivalry between materials provide strong impetus for lower cost aluminum smelting processes.

Competition Within the Industry

Aluminum commodity ingot prices have fluctuated by a factor of almost two on several occasions in recent years (Figure 1), forcing the permanent closing

of many production facilities. Among the causes are excess capacity, global marketing of aluminum through commodity exchanges, disparate power costs in different locations, distorted currency exchange rates, and policies in some nations to maintain employment and trade balances regardless of direct cost/price relationships.



Aluminum Prices

Figure 1

Competition With Other Materials

Historically, aluminum markets have grown principally by penetrating the markets of other materials

with price reductions made possible through technical advances. Shortly after aluminum first sold in Europe in the 1850s, the price of aluminum dropped and its use as a semiprecious metal grew as sodium replaced potassium for reducing aluminum chloride [1]. By the time the Hall-Heroult process was implemented the price had dropped well over 100-fold [2] from the 1850 price and aluminum began to compete more strongly with the more common metals. Cost reductions through efficiency improvement, increased productivity and economies of scale permitted aluminum to cross under the cost of copper (equal volume basis) in the 1890s and under zinc (equal volume basis) in the 1930s, and share in the markets of these metals. Price competition has heightened and aluminum production grown in recent years as aluminum is penetrating markets in which inexpensive plastics, glass and steel also compete. However, the usual flow of improvements in performance and costs in Bayer/Hall-Heroult technology has been unable to offset the periodic lows in commodity ingot prices in recent years. In fact, conventional Bayer/Hall-Heroult may be approaching real lower limits in costs. This has led to considering changes in the aluminum smelting process that would permit profitable operation through the whole commodity ingot price cycle.

Extraction Experience for Metals

Guidance on cost reduction possibilities can be obtained by examining price information for 46 metals in Figure 2 [3]. The principal factor determining metal price (pound mole basis) is average abundance in the earth's crust. Prices increase more than 100,000-fold while abundance drops more than 10 million-fold. Within the broad band of points for individual metals the price/abundance relationship breaks into a number of separate curves for different extractive technologies. Price differentials are also evident for metals in the earlier stages of commercialization before learning curve advances or economies of scale are realized. Price cartel activity is evident for tin. Metals that are produced by thermal methods have the lowest market price for their abundance while electrolytically produced metals are priced 4 to 23 times higher, the factor increasing as the abundance falls off. Metals that have more stable oxides are more difficult to reduce carbothermally because of vaporization and side reaction problems at

the higher temperatures required and have been produced electrolytically for this reason. Reducing the vaporization and side reaction problems for these metals should drop their costs nearer to those now produced thermally, allowing for the higher energy and temperature requirements.

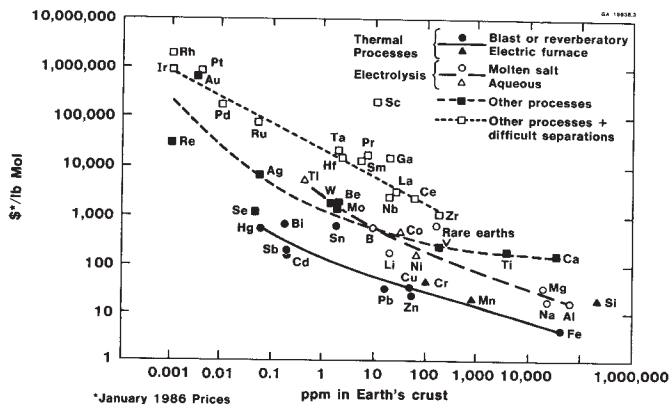


Figure 2

Cost Sectors

Another approach to identifying technical opportunities for cost reduction is to examine cost sectors in the Bayer/Hall-Heroult process. The largest sectors include ore, energy, capital, and labor followed closely by carbon, casting, other materials and repair maintenance, administrative sales, taxes, and insurance [4]. These costs are directly tied to technical features of the process. Direction and magnitude of cost changes for alternate processes are indicated from energy sources, ores, efficiencies, material costs, productivities (as related to labor and capital), and capital needs (as related to number of process steps, temperature, and concentration of the process stream).

No alternate process is likely to be implemented unless it can operate profitably through the bottoms of the commodity ingot price cycle while continuing to pay off the investment costs of new facilities. As a rough approximation, costs of an alternate process would have to approach almost half of average Bayer-Hall-Heroult costs for this to happen today. Since no single cost factor in aluminum production today amounts to half of the production costs, the alternate process that meets the need will have to strongly reduce a number of larger cost sectors.

Energy Cost

Most of the search for alternate processes has centered around reducing energy requirements, justified by the 20-40% of domestic costs [5] that energy represents and the good prospects for improving upon the 45% overall energy efficiency of the electrolytic process [6] and the 33% efficiency in generation of electricity from steam. However, even if the energy cost sector was totally eliminated, cost reduction in other cost sectors would still be required to make operations profitable during market lows.

Any process that starts with alumina and ends with aluminum has the same theoretical energy requirements. The actual energy requirements are greater than these, depending on the efficiencies of the chemical steps between alumina and aluminum.

Alumina

Smelter grade alumina is one of the largest items in the cost of aluminum production. Processes that combine reduction and purification may permit the direct use of unpurified ores in the place of alumina. This could offer opportunities for cost reduction if less costly ores can be used and/or by-products can be produced with values equaling or exceeding their production costs. However, this approach can drive up production costs and capital if production steps are added, the process stream has to go through dilute phases (gases or dilute liquids), or if special disposal of impurities is required.

Capital and Labor

The productivity of a modern Hall-Heroult cell is about 0.0014 volume of metal per hour per unit cell volume [6], about one-tenth the productivity of an iron blast furnace [7]. This difference occurs because metal is produced in a three-dimensional zone of the blast furnace and only on the planar cathode area of the Hall-Heroult cell. The 14-bipolar cell of the Alcoa Smelting Process bridges the gap between the Hall-Heroult cell and the blast furnace with a productivity of 0.004 volume of aluminum each hour per unit cell volume [6]. These productivities have a strong effect on capital and labor requirements, which are among the largest cost sectors in aluminum production.

Other electrolytic processes for which nonconsumable anodes exist, or could be developed, would benefit from bipolar cell configurations with possible gains in productivity over Hall-Heroult cells. These possibilities will be discussed.

Other strong influences on capital are process complexity and process stream volume. Adding process steps usually adds capital, labor, and operating costs. Conversely, combining steps can reduce capital needs, labor and operating costs. Flow charts that involve putting the process streams into dilute phases such as gases and solutions entail large increases in process stream volume. This, in turn, increases capital needs and operating costs for the equipment to contain larger stream volumes and for the energy and equipment for producing the phase changes and separations. Higher temperatures usually increase operating and capital costs, but these may be offset by other considerations to be discussed.

Carbon

Carbon is another reactant that could present a cost reduction opportunity in Hall-Heroult smelting if an alternative method combined separate reduction and purification steps. Coal or metallurgical coke is usually less costly than the petroleum coke and coal tar pitch now used in formulating carbon anodes for the Hall-Heroult process. The ash in coal and metallurgical coke contains substantial quantities of aluminous materials that could supplement the alumina-bearing ores. The nonaluminous ash components or their reduction products could be removed in the purification step.

Energy Sources

Three sources of energy are commonly employed to meet the theoretical energy needs, ΔH , for the reduction of alumina. They are electrolytic, chemical, and thermal. Thermal energy is required for all processes. It may: (a) be the sole source, (b) be paired with a chemical reductant or electrolysis, or (c) be combined with both of these. The theoretical electrolysis energy is supplied by passing the coulombs required by Faraday's Law at the theoretical voltage for electrolysis of the aluminum compound to aluminum. The chemical source is usually carbon, but

in the early industry it was sodium or potassium, which were used to reduce the aluminum chloride that had been produced from alumina. The theoretical thermal energy, $T\Delta S$, that must be supplied at temperature for isothermal operation is related to ΔG , the theoretical free energy supplied by electrolysis and the theoretical ΔH by Equation 1 as diagrammed in Figures 3, 8 and 9 for the various processes.

$$\Delta H = \Delta G + T\Delta S \quad (1)$$

The thermal energy is in addition to heat required to bring the reactants to temperature. The source of the thermal energy can be electrical, combustion, or inefficiencies in the other two sources, the carbon reductants or electrolysis.

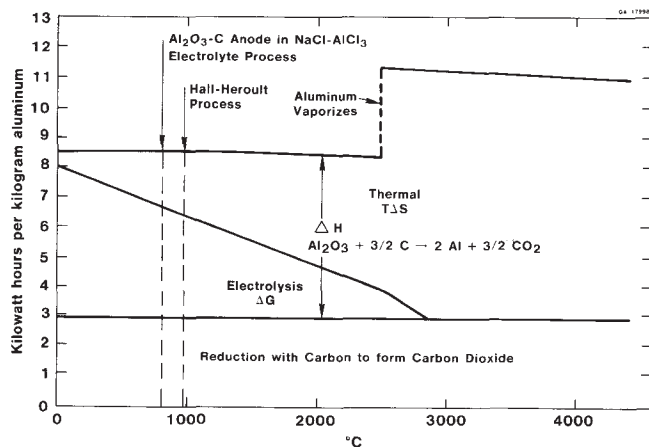
Three kinds of information are helpful in considering the direction and magnitude of changes in energy costs from process to process. These are: distribution of the theoretical energy needs between these three sources, the relative costs of these energy sources, and the average efficiencies in using the sources. These will be presented in the discussions of a number of processes, which are arranged by types and energy sources. Within each set of energy sources the processes are discussed in order of increasing number of process steps.

Electrolytic Processes

Electrolytic-Carbon-Thermal Energy Sources

Bayer/Hall-Heroult Process. The theoretical energy needs in this base case are met from three sources: (a) the carbon anodes that are oxidized (essentially to carbon dioxide); (b) the decomposition free energy supplied by electrolysis; and (c) thermal energy from polarization, resistance losses, reoxidation of products and air burning of carbon. The theoretical energy is shown in Figure 3 for the reaction of alumina to form aluminum and molecular oxygen at different temperatures. A vertical line at the temperature of the Hall-Heroult process breaks the total theoretical 8.69 kWh/kg Al (18.5 kWh/kg Al operating average) into three segments. About 3.1 kWh (35%) of the total is met by the carbon anode oxidizing to carbon dioxide, 3.5 kWh (40%) from electrolysis, and the remaining 2.1 kWh (25%) from thermal

sources. The theoretical voltage for Hall-Heroult electrolysis is proportional to the height of the vertical dotted line through the "electrolysis" segment of Figure 3. The actual thermal energy available from resistive losses, reoxidation of product, polarization, and burning of carbon in modern Hall-Heroult cells (Figure 4) far exceeds the needs for thermal energy; only about one-fourth of it can be used productively within the process at temperature [6]. A small amount (0.7 kWh/kg Al) can be used to bring the reactants to temperature, a little more to supply reaction heat, and the remainder purposely lost from the cell.

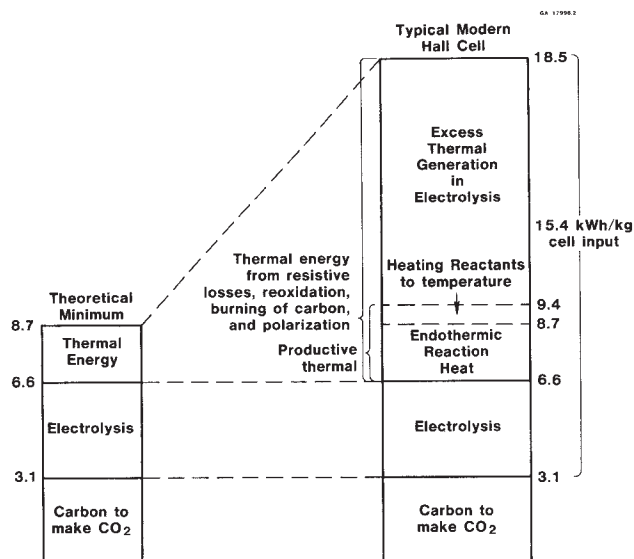


Theoretical Energy Requirements to Produce Aluminum from Alumina at Temperature Including Energy from Carbon Reducing Agent that Forms Carbon Dioxide

Figure 3

The efficiency in using carbon in the Hall-Heroult cell is about 75%. This compares to only 45% for electricity. Furthermore, the capital required per unit of energy increases in the ratio 1:4:16 in going from combustion to chemical reductants to electrical power for energy sources [8]. Moving to processes that get more of their energy from combustion and reductants and away from electricity should increase efficiency and reduce costs, including capital. A great deal of the effort on Hall-Heroult process improvements is spent on reducing the production of this excess thermal generation. This includes reducing anode-cathode separation, limiting all other voltage drops, and reducing reoxidation and air burning.

Another possibility is to raise the temperature for electrolysis in Figure 3 (shifting the vertical



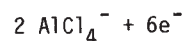
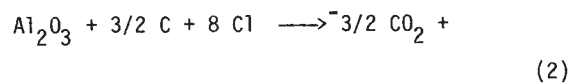
Hall Process Energy Requirements kWh/kg Aluminum at Temperature

Figure 4

dotted line to the right), reducing the voltage requirement, possibly also reducing polarization, and increasing the capacity for productive use of thermal energy. Less of the thermal energy would have to be wasted. Thus, contrary to conventional wisdom, thermal efficiency would increase. Of course, formation of carbon monoxide may be favored at higher temperatures, which would increase carbon requirements. Also, reoxidation usually increases at higher temperature but reformulation of the electrolyte might overcome this. Calcium fluoride-rich electrolytes with good ionic conductivities, high alumina solubilities, low volatilities, and low reactivities with water vapor, carbon, and aluminum are good possibilities.

Bayer/Al₂O₃-C Anode in Chloride Electrolyte.

Alumina can be electrolyzed several hundred degrees lower than in the Hall-Heroult process by employing an alkali metal-aluminum chloride electrolyte, which is more conductive than the electrolyte in the Hall-Heroult process [9]. The alumina is contained in the carbon anodes and is converted to aluminum chloride in the electrochemical reaction without detectable evolution of chlorine.



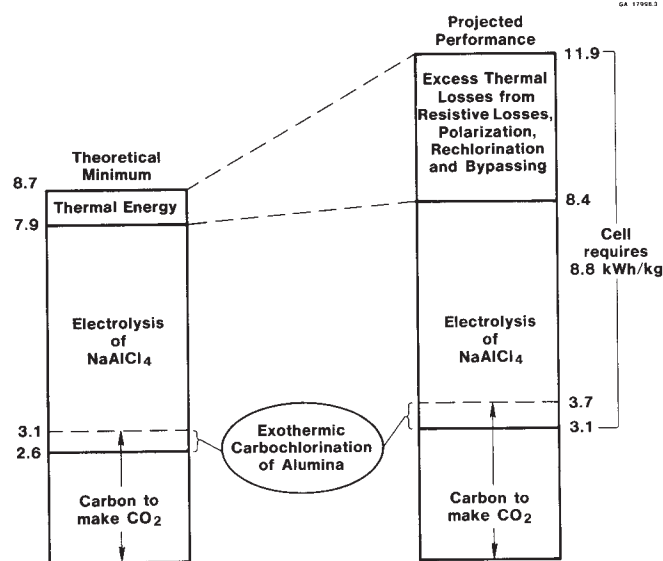
The decomposition voltage is slightly higher than in the Hall-Heroult cell because of the lower temperature. The anodes are more resistive than in the Hall-Heroult cell because they contain up to 85% alumina to meet the stoichiometric requirements. This voltage drop may be decreased by incorporating vertical spikes of carbon or aluminum in the anodes. While resistive losses may be higher than in the Hall-Heroult cell, lowering the temperature (as in Figure 3) decreases the capacity of the process to use excess thermal energy productively within the process.

Electrolysis of Aluminous Ores/Alloy Separation and Purification. One way to circumvent the cost of the Bayer process, and possibly dependence on bauxite, is direct electrolysis of aluminous ores in Hall-Heroult bath. In principle, staged electrolysis should permit separation of the metal components of an ore in a sequence such as iron, silicon, titanium, aluminum, magnesium through to calcium. However, overlapping deposition of the different metals occurs due to alloying, compound formation, and polarization at practical current densities. Selection and blending of ores allow production of Al-Si [10] and other commercially valuable compositions. Pot ledging and mucking can be controlled by adjusting oxide concentration in the bath. A 0.5% loss in current efficiency was obtained for each 1% Si in the product. The cost of producing these alloys electrolytically with pure carbon anodes in a Hall-Heroult cell at 45% thermal efficiency must be compared with costs in two other alternatives. One is to produce the same alloys by carbothermic reduction in an electric or blast furnace, as described later. The other is to prepare the same composition from scrap metal or from alloying of the pure metals.

These alloys may also be purified electrolytically or thermally. However, purification of alloyed metals by electrolytic or thermal methods is usually more expensive than hydrometallurgical purification of ores unless valuable by-products are produced to offset costs of the vacuum processing, electrolytic

processes and/or higher temperature operations that are often involved.

Bayer/Carbochlorination/Bipolar Cell. The Alcoa Smelting Process adds a third chemical step in which alumina is converted to aluminum chloride by carbochlorination [9,11-16]. This permits carbon electrodes to be used as inert electrodes in a bipolar cell in which chlorine is produced at the anode to be recycled to the carbochlorination step. By using close anode-cathode spacing and a highly conductive electrolyte, the thermal generation is reduced about 70% in the bipolar cell compared to Hall-Heroult cells for a projected overall requirement of 11.9 kWh/kg for 73% efficiency, as shown in Figure 5. The carbochlorination reaction can be exothermic but the decomposition potential for electrolysis is raised by about 0.7 V. The thermal generation occurs principally from resistive losses and current bypassing bipolar electrodes. Polarization and rechlorination are low.



Alcoa Smelting Process Energy Requirements kWh/kg Al at Temperature

Figure 5

The principal advantages of the process are substantial reduction of energy needs and capital reduction through productivity gains, both achieved with the bipolar cells. Partially offsetting these advantages is the added carbochlorination step with its capital requirements and difficulties in maintaining efficient cell performance over long periods. Since the carbochlorination step uses gaseous feed

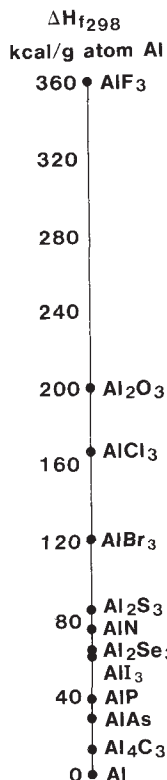
(Cl₂) and produces a gaseous product (AlCl₃), the volume of this process stream is large. For flexibility and reliability the cell and carbochlorination systems can be operated independently though this increases costs and energy consumption. The projected cost savings are mainly in two cost sectors, energy and capital. The overall savings are insufficient to offset the lows in commodity ingot prices.

Carbochlorination of Ore/Separation and Purification of Metal Chlorides/Bipolar Cell.

Carbochlorination of raw aluminous ores [17] to make aluminum chloride for a bipolar cell has the possible advantages of metal chloride by-product from the impurities in the ore, avoidance of Bayer process costs, and freedom from dependence on bauxite. Chlorination of the silica can be suppressed and titanium tetrachloride, the most valuable product, can be readily separated. Removal and disposal of ferric chloride is costly. Furthermore, the process stream volume is large because both reactants and products are gaseous. This, together with the processing of by-products and the higher temperatures compared to the Bayer process, makes costs and capital requirements much higher than for the Bayer process. The value of the titanium tetrachloride by-product does not adequately offset these increased costs. The idea of finding a cheaper way to produce aluminum chloride for a bipolar cell still deserves attention, but accomplishing this by carbochlorination of aluminous ores with large process gas volumes and difficult separations of products is challenging.

Bayer/Carbonitridation or Carbosulfidation/Electrolysis of AlN or Al₂S₃.

Electrolysis of aluminum nitride [11,17] or aluminum sulfide [9,11,12,17] may also offer the advantage of bipolar cell operation with carbon electrodes. The potential advantage over a bipolar cell for electrolyzing aluminum chloride is the lower theoretical voltages required, 0.8 V for aluminum nitride and 1.1 V for aluminum sulfide compared to 1.9 V for aluminum chloride. This can be seen in Figure 6 where the ΔH_{f298} of various aluminum compounds are plotted on the linear scale extending from AlF₃ at the top to pure aluminum at the bottom. The distance along the scale from Al₂O₃ to any compound represents the ΔH_{f298}, which must be supplied from energy sources. Carbon and alumina can be used with chlorine, bromine,



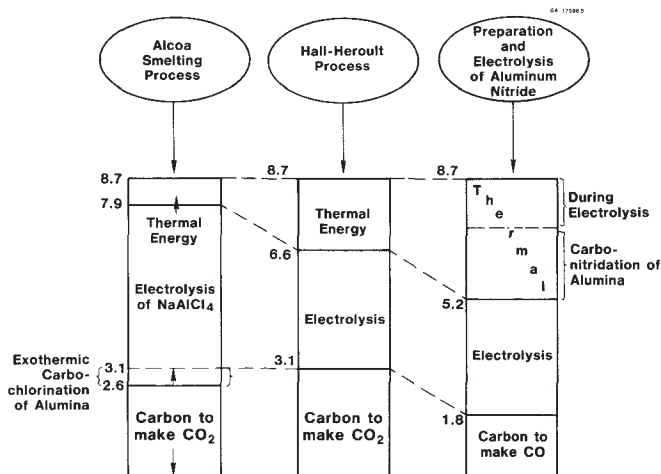
Energy Scale for Aluminum and Its Compound

Figure 6

nitrogen, iodine, or sulfur to form the corresponding aluminum compound. The nearer the compound is to aluminum the lower the voltage for a sustained electrolysis of the compound to aluminum under isothermal conditions. However, the sum total of the theoretical energies for the two steps, conversion of alumina to the compound and electrolysis of the compound to produce aluminum, has to be the same for all the compounds. Because the electrolysis voltage for aluminum nitride is lower than for aluminum chloride, a greater thermal energy input is required in carbonitridation of alumina than in carbochlorination of alumina.

Figure 7 contrasts the theoretical energy requirements for three processes: the Alcoa Smelting Process, the Hall-Heroult Process, and the preparation and electrolysis of aluminum nitride. In this order the decomposition voltages decrease and the thermal energy needs increase. While carbochlorination of alumina is exothermic and proceeds rapidly below 1000°C, the carbonitridation is endothermic and requires temperatures near 1700°C. Carbosulfidation

requires still higher temperatures, is still more endothermic, and is complicated by side reactions. Finding suitably conductive solvents for aluminum nitride and aluminum sulfide is also a problem. Solubilization of AlN in cryolite as $Li_3N \cdot 3AlN$ has been suggested [11]. Fluorides or chlorides may serve for dissolving aluminum sulfide. The cost advantages will probably be in cell energy and cell productivity as in the Alcoa Smelting Process, with offsetting cost increases in producing the sulfide or nitride. The potential advantage will probably be no more than for the Alcoa Smelting Process.



Theoretical Minimum kWh/kg Aluminum to Convert Alumina to Aluminum in Processes Using Three Energy Sources at Temperature

Figure 7

Electrolytic-Thermal Energy Sources

Electrorefining of Alloys. One of the purification processes that can be used with any of the extractive technologies that produce aluminum alloys is electrorefining. The best known version of this is the Hoopes process [18] in which the alloy is the anode at the cell bottom and the aluminum is electrolytically extracted away from the more noble impurities and deposited at the floating aluminum cathode. Barium salts are added to raise the density of the cryolite electrolyte so pure aluminum floats. If the alloy to be purified is not dense enough to sink in this electrolyte, copper is added. The Hoopes process was first used to purify aluminum alloys produced by carbothermic reduction. The anode metal and cathode metal are kept 12 cm apart to prevent remixing. This causes high voltage drops through the electrolyte,

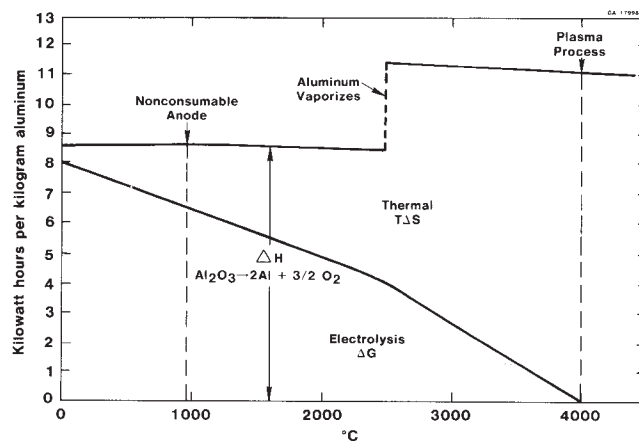
which became less conductive with the addition of barium salts to adjust density. Current densities have to be relatively low (0.4 A/cm^2) because of the low conductivity, and the process uses about as much electrical energy (15 kWh/kg) as the Hall-Heroult process with current efficiencies of 93%. Since costs are higher than for Hall-Heroult cells, the process is only used at present to produce 99.999% aluminum from Hall-Heroult metal.

The use of porous diaphragms to contain the molten aluminum alloys for electrorefining potentially solves many of these costs and energy problems but has not been carried beyond bench development [18,19]. The diaphragm permits the use of less dense, more conductive electrolyte at low anode-cathode separations. Because no gas is evolved in the electrolysis, current densities can be several times higher (5 A/cm^2) than in Hall-Heroult cells and voltages are low if the diaphragm is porous enough. Woven graphite and silicon nitride cloths have been used successfully as diaphragms in bench tests. Impurity concentrations have been reduced by 1000-fold in a single pass at current efficiencies of 96%.

The purification of alloys after reduction of mixed oxide ores may have difficulty competing with purification of ores before reduction. The purification of ores by hydrothermal processes such as the Bayer process or the acid leach process is more productive and less costly. Electrorefining processes are planar processes with comparatively low productivities, even when conducted at high current densities. Furthermore, the cost of the energy and carbon reductant expended in reducing the impurities may or may not be recovered in any by-product values.

Bayer/Nonconsumable Anode Cell. One of the possible improvements is electrolysis of alumina with a nonconsumable anode [9,11-13]. The advantages are: (a) no carbon anode expense, (b) no anode changing, with the consequent thermal upsets that interfere with cell control, (c) dimensionally stable anode faces for closer control of anode-cathode spacing and resistive losses, (d) lower anode polarization voltages, (e) by-product oxygen, and (f) sealed cells for closer control of fumes and smaller, less expensive fume control systems. The penalty for not using carbon (Figure 8) is the higher decomposition voltage,

2.21 V, although this is partly offset by the lower polarization voltage. A key issue is whether the energy for converting alumina to aluminum is supplied at lower cost with carbon or electricity. For cells with 45% power efficiency, 6.8 additional kWh must be used for each kilogram of aluminum produced if nonconsumable anodes are used. However, this power penalty can be greatly reduced by using thin nonconsumable anodes with less resistance than carbon anodes, reducing anode-cathode separation and better cell control. The potential saving is the cost of Hall-Heroult carbon anodes less the cost to make the nonconsumable anodes, the value of the by-product oxygen, and a savings in capital for simpler fume systems and smaller anode manufacturing facilities. The nonconsumable anode could become a more economical process if carbon costs were to increase relative to costs of electricity, especially for sites that have very low power costs. Cermet materials in the Ni-Fe-Cu-O system have suitable electrical conductivity and have produced aluminum that approaches commercial purity in bench tests [20].



Theoretical Energy Requirements to Produce Aluminum from Alumina at Temperature by Decomposition to Oxygen

Figure 8

Bayer/Bipolar Hall-Heroult Cell. This is a process that should have the energy efficiency and productivity of the Alcoa Smelting Process but involves only two chemical steps in place of the three in the Alcoa Smelting Process. The key is the development of a bipolar material that resists oxygen on its anode side and aluminum on its cathode side. This is a challenging problem requiring an electrode

that can resist oxygen potentials differing by a factor of 10^{34} on its two faces, and yet remain conductive and sound for long periods at elevated temperatures. A single material, carbon, meets this need in the Alcoa Smelting Process, with chlorine activities differing by 10^{19} on the two faces of the bipolar electrode. The theoretical energy requirements are the same as for the nonconsumable anode shown in Figure 8. This process should have the energy advantages of the Alcoa Smelting Process but with lower capital (because carbochlorination is avoided), provided the bipolar electrodes are not too costly and have long lives.

Carbothermic Processes

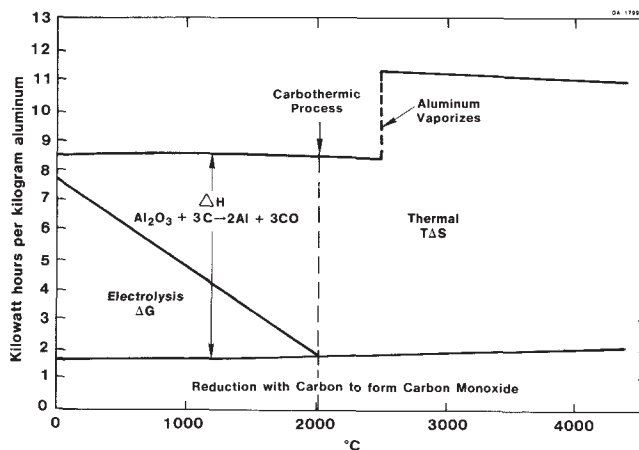
Carbothermic Reduction of Impurities (in ore) to Replace the Bayer Process

One of the processes developed and used commercially for purifying aluminous ores in the earlier part of the 20th century was the dry process [21]. Aluminous ore was heated with sufficient carbon in an electric arc furnace to reduce just the impurities. A ferrosilicon base alloy containing the other impurities formed first, and when the alumina fused at still higher temperatures the fused slag and molten metal each coalesced and separated by density differences. Impurities in the slag were further leached with acid but the process never competed well with the Bayer process.

A later improvement on the dry process, known as the Pedersen process [21], was used commercially for at least 40 years to treat ores not amenable to the Bayer process. A mixture of carbon, lime, and high iron-low silica bauxites was heated in an electric arc furnace. Pig iron was produced, leaving a calcium-alumino-silicate slag rich in alumina. Sodium aluminate was extracted from this slag by leaching with a sodium carbonate solution containing a small amount of sodium hydroxide. Since these processes deal with condensed phases rather than gases, they may represent a lower capital alternative than carbochlorination to Bayer processing of bauxites. They are commercial processes while carbochlorination has not been used commercially to produce aluminum.

Bayer/Carbothermic Reduction

The interest in carbothermic reduction is driven by two advantages: (a) much higher productivity than in electrolytic processes, and (b) higher energy efficiencies. Thus, two of the largest cost sectors, energy and capital, are addressed. The thermal efficiency of iron-making furnaces approaches 80%, which is well beyond the 45-47% typical for Hall-Heroult cells. Furthermore, if carbon combustion can be used as an energy source there is a further gain in avoiding the inefficiency of generating electricity from thermal energy. The theoretical energy for the reaction is shown in Figure 9. The reaction of alumina with carbon begins near 1950°C to form a liquid aluminum oxycarbide in which Al_4C_3 dissolves in alumina [22].

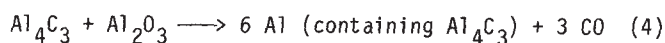


Theoretical Energy Requirements to Produce Aluminum from Alumina at Temperature Including Energy from Carbon Reducing Agent that Forms Carbon Monoxide

Figure 9



Continued reaction increases the Al_4C_3 concentration in the first liquid as the temperature is increased. If the free carbon is exhausted, the first liquid will decompose, evolving more CO near 2050°C to form a second liquid of Al_4C_3 dissolved in aluminum, which floats on the first liquid.

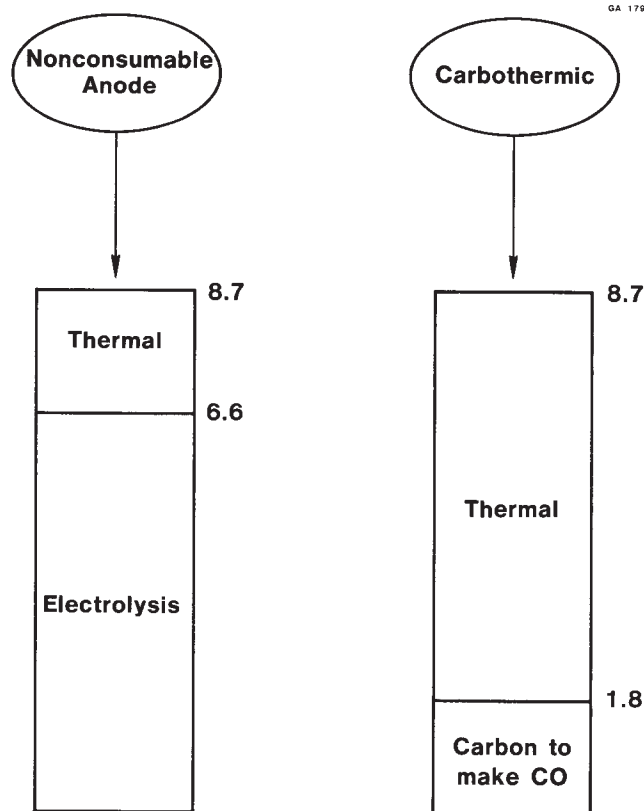


Steadily increasing temperatures are required to keep the first liquid reacting to form the second liquid as the Al_4C_3 contents of both the first and second liquids drop. As the second liquid is cooled, Al_4C_3 precipitates and it is necessary to either coalesce the liquid aluminum with fluxing agents or to strip the Al_4C_3 from the aluminum with an alumina-rich slag [23]. Vaporization of aluminum and aluminum suboxide (Al_2O) occurs as CO vapors from the reduction sweep the reaction zone, particularly at higher temperatures when the final one-third of the overall CO is evolved as the second liquid forms. Vaporization sharply decreases yields unless the vapors pass countercurrent to incoming solid reactants [24]. Countercurrent flow serves to preheat the incoming reactants and recover the material values from the vapors. The extent of vaporization exceeds the needs for preheating. Vaporization can be reduced by preventing the carbon monoxide from the reaction that forms the first liquid (two-thirds of overall CO evolution) from sweeping the area of the second liquid. This can be accomplished through staging of the reaction by either forming the two liquids at different times or not allowing the vapors in forming the first liquid from sweeping the area where the second liquid forms [24,25].

Another approach to the vaporization problem is to let the aluminum and suboxide vapors react with carbon to form aluminum carbide, which is subsequently decomposed in vacuum to aluminum vapor and carbon [26]. The thermal energy source can be electrical, either from an arc [23], resistive heating of the oxycarbide slag [24], or a plasma. In situ combustion of carbon cannot ordinarily be employed as the heat source because the additional carbon monoxide would vaporize most of the product. In Figure 10 the theoretical energy needs for carbothermic reduction are contrasted with those for the nonconsumable anode, another process using only two energy sources. The thermal energy component for carbothermic reduction is almost four times as great as with the nonconsumable anode.

Carbothermic Reduction of Ore/Alloy Separation

Carbothermic reduction of ore is another means for avoiding the costs of alumina--and possibly bauxite. Most often aluminum is extracted from the alloy that forms, but in a few cases the alloy is



Processes Using Only Two Energy Sources
Theoretical Minimum Energy kwh/kg Aluminum at
Temperature

Figure 10

proposed for commercial application. The alloy helps to solve the vaporization and back reaction problems by reducing the aluminum activity.

There has been much work on producing aluminum alloys by carbothermic reduction in arc furnaces. In fact, the Cowles Brothers' process, which preceded the Hall-Heroult process, produced crude aluminum-copper alloys by this method [1]. In the U.S.S.R. [27] improved yields have been achieved by blending ores to reach an optimum Al/Si ratio.

Alcan undertook a major effort in the 1950s to produce an Al-Fe-Si alloy in an arc furnace and then to extract aluminum from it, employing the mono-chloride process discussed under "Thermal Processes." Finding materials that could hold up in the aluminum chloride atmospheres was a major problem. The potential advantages were avoidance of Bayer costs, higher productivity, and lower capital in the reduction step. Disadvantages were high capital and material problems

in the monochloride refining stages where gaseous reactants and products were employed at elevated temperatures in vacuum.

Reynolds Metals also was involved in producing Al-Si alloys in arc furnaces for use in castings [28].

Ethyl Corporation [29], U.S.A., proposed the idea of producing Al-Si-Fe alloys in blast furnaces and then extracting aluminum from the alloy with aluminum tripropyl, as will be discussed under "Thermal Processes." The advantage of the blast furnace is avoidance of the inefficiency and cost in generating electricity for an electric furnace. The additional carbon monoxide sweep-gas from in situ combustion can further aggravate the vaporization problem unless the aluminum activity is sharply lowered by alloying. Efficiently providing the needed reaction heat from a combustion source for a process near 2400°K is difficult. If the carbon and oxygen are not preheated, only about 32% of the combustion heat is theoretically available to supply reaction heat at 2400°K. By preheating the carbon to 2400°K the theoretical efficiency in supplying reaction heat at 2400°K increases to 63%. Preheating of carbon to 2400°K can be accomplished by flowing the off-gases counter-current to the carbon-containing charge. If a suitable containment system could be found for preheating oxygen with off-gases, the theoretical efficiency in supplying reaction heat at 2400°K from carbon combustion would approach 93%.

The Aluminum Company of America developed a pilot unit to attempt to produce Al-Si alloys in a blast furnace but was hampered by bridging problems from the reflux of metal and suboxide vapors [30,31]. The addition of iron improved operations by reducing reflux. Supplying a significant portion of the energy as electricity in either a one- or two-step blast arc seemed to offer some promise.

The Mitsui Corporation heads a national project in Japan to produce Al-Fe-Si alloys in a blast furnace using lead to reduce the aluminum activity [32]. As discussed later, the lead-aluminum alloy disproportionates on cooling to produce a lead-rich fraction and an aluminum-rich fraction, but the aluminum fraction requires purification for commercial use. The National Chemical Laboratory for Industry in

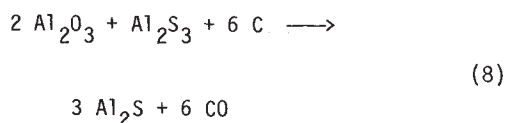
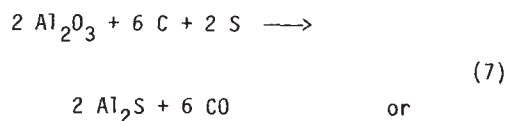
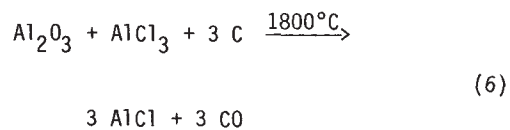
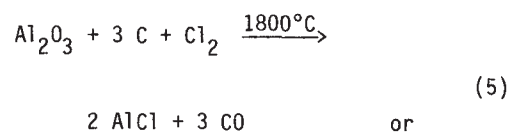
Yatebea, Japan, has succeeded in producing Al-Fe-Si alloy in a pilot blast furnace without supplemental heat [33]. Yields and aluminum contents were low but were enhanced by adding lime to the charge.

Although carbothermic processes to produce aluminum alloys using in situ combustion heat sources have not been fully demonstrated, this approach has potential advantages in energy efficiency, productivity, and less expensive ore sources. Since the processes seriously lack inexpensive means for purifying the alloys, they may be implemented only if alloys of commercial value can be produced.

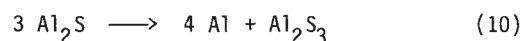
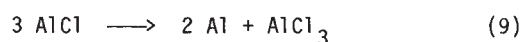
Bayer/Carbonitridation, Carbochlorination or Carbosulfidation/Thermal Decomposition or Disproportionation

Dissociating a compound is a further use of thermal energy in processes. When aluminum nitride, formed by carbonitridation of alumina, is heated to 1700°C, a vacuum at 0.5 torr dissociates the nitride into aluminum and nitrogen [11].

Carbochlorination or carbosulfidation of alumina at higher than normal temperature produces subvalent forms of aluminum chloride and aluminum sulfide [11].



Cooling of the vapor can cause the subvalent aluminum gases to disproportionate to form aluminum liquid and the trivalent aluminum compound as discussed under "Thermal Processes."



The difficulty with these processes is that the other products of the decomposition or disproportionation are also gases and the back reaction can occur just as readily upon cooling. Shock cooling of the vapor may reduce back reaction to some degree but is usually energy inefficient. Furthermore, all of the aluminum must pass through the vapor phase, which increases process stream volume and raises capital and operating costs.

Bayer/Carbothermic Reduction of Alumina to an Alloy or Compound/Extraction of Aluminum

One means to suppress vaporization when carbothermically producing pure aluminum from alumina is to introduce lead [32], tin [34], or other elements [35] to reduce aluminum activity. Lead was chosen because its alloy with aluminum disproportionates into a lead-rich fraction and an aluminum-rich fraction on cooling. However, the aluminum-rich fraction still requires purification by the methods discussed in Thermal Processes for commercial use. Furthermore, looping the lead or tin between reduction temperatures and lower temperatures with a small percentage of aluminum on each cycle increases energy needs.

Carbochlorination of Clay/Separation of Metal Chlorides/MnCl₂ Oxidation/Mn Blast Furnace/Mn + AlCl₃ Reactor

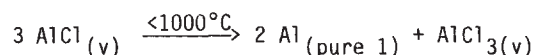
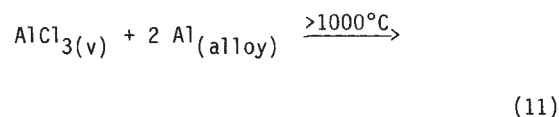
The original Toth process [9,11,12,15,17] involved carbochlorination of clay to produce aluminum chloride and separation of the aluminum chloride from the other chlorides that form, as described previously. The aluminum chloride was then reduced with manganese at 230°C and 4 torr pressure to produce manganese chloride and aluminum of low manganese content. To close the loop, the manganese chloride

was oxidized at 600°C and the manganese oxide carbothermically reduced in a blast furnace at 1750°C. Three of the steps are quite difficult. These are the reaction of manganese with aluminum chloride, the oxidation of manganese chloride, and the production of pure manganese in a blast furnace. The involvement of five chemical steps, the gaseous products in the carbochlorination, the difficult steps already mentioned, and the need to purify the product for most uses greatly increases capital needs and costs.

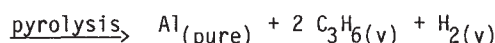
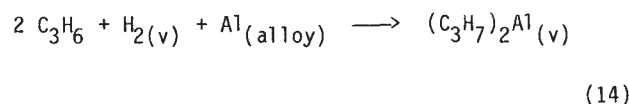
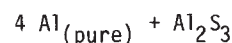
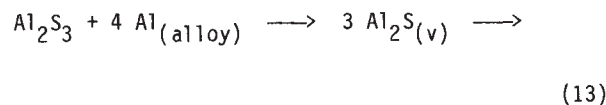
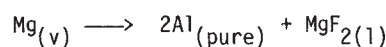
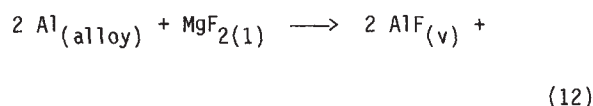
Thermal Processes

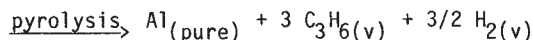
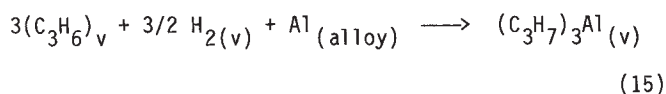
Disproportionation of Aluminum Halides, Sulfides, or Tripropyl Aluminum

Aluminum can be extracted from aluminum alloys or aluminum compounds of low stability by forming gaseous subvalent compounds that disproportionate on cooling to the normal valence compound and free aluminum [9,11,12,14,36]. The equations are:

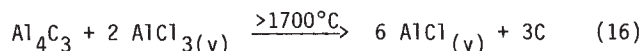


Similar reactions are possible with other compounds.

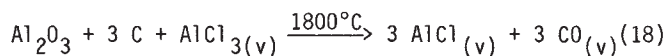




These reactions are only practical for extracting aluminum from compounds or alloys with activities of 10^{-2} or higher. The reaction of $AlCl_3$ with Al_4C_3 is >90% above 1700°C at 1 atm pressure.



These reactions can be extended to extracting aluminum from more stable compounds by adding a reducing agent such as carbon to the reaction



The difficulty is back reaction of the CO and $AlCl_3$ upon cooling. The processing of all the aluminum through the gas phase greatly enlarges the process stream volume and involves introducing and removing heat with the attending increases in capital and operating costs.

Selective Solution in Volatile Metals

One class of alloy purification processes that was used during World War II in Germany for reclaiming aluminum was selective solution of scrap in volatile metals that form low temperature eutectics with aluminum. They used magnesium but the process also works with zinc and mercury (Table I) [18]. These processes could be used to purify alloys formed by electrolysis or carbothermic reduction. All of these processes are based on dissolving the aluminum in the metals at or near the melting point of aluminum (under pressure for mercury), lowering the temperature into the eutectic range to precipitate the impurities as insoluble intermetallics, filtering out the intermetallics, and then distilling the volatile metal from the aluminum. Most impurities except copper, nickel, and tin were effectively removed. The capital

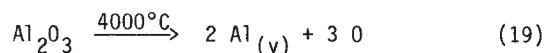
requirements are high because of the need to vaporize, condense, and process large volumes of metal.

Table I. Technologies for Refining and Purifying Aluminum Alloys by Selective Solution in Volatile Metals

Volatile Metal	Furthest Stage of Development	Typical Aluminum Product
Mercury	Pilot	Al and Cu contents proportional to initial charge composition
Magnesium (Beck)	Commercial	Al, Cu and Ni contents proportional to initial charge composition
Zinc	Pilot	Al and Cu contents proportional to initial charge composition

Bayer/Plasma

The only process that can produce aluminum from alumina with only one energy source is thermal dissociation of alumina in a plasma [9,11] above 4000°C.



The energy requirements given in Figure 8 are higher than for the other processes because the aluminum vaporizes. The further dissociation of the oxygen into atoms probably requires more energy than shown. The difficulty is poor thermal efficiency because of the high radiant energy losses to the condenser used to quickly cool the aluminum to prevent back reaction with the oxygen. Capital requirements should be very high because of the high temperatures and gaseous reactions.

Technology for Competing

None of the described processes are likely to have greenfield costs below the lows in the aluminum commodity ingot price cycle. This would require cutting the average greenfield cost of production by almost 50%. The range of characteristics of hypothetical processes that might meet this goal can be described. Nearly every major cost sector would have

to be addressed. Such a process would probably have just two steps, a combined smelting and ore refining step, as does iron making, and possibly a metal purification step. Passing the production stream through the gaseous stage should be avoided; electrolytic cells should not be used unless they are bipolar, operate at high current densities or produce products with high electrochemical equivalent weights. Pyrometallurgical steps should be preferred because of high productivity, energy efficiency, and low capital. Less expensive forms of carbon such as metallurgical coke or coal would be preferred; hydro-generated electricity or thermal energy from in situ combustion should be favored. Ores less expensive than bauxite would be desirable, and any by-products should sell for more than their production costs.

Processes that meet these criteria could allow aluminum to compete much more strongly with steel, plastics, and glass and to probably undergo major growth in use. Although the theoretical energy to produce a unit volume of aluminum is about 50% higher than for iron, the present cost difference lies mostly in the lower productivity, separate purification/reduction steps, lower energy efficiency, and more expensive energy form for making aluminum by the present technology.

Aluminum as the most plentiful metal in the earth's crust has a strong chance to more closely approach the cost of the heavier metals, particularly if a process that uses a thermal energy source can be developed. If this were to be accomplished, aluminum would more strongly share in the ten times larger market of the heavier metals and in the markets for glass and plastics. Nearly all transportation applications, metal containers, exposed structures and outdoor hardware would be much more open to the use of aluminum.

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