

Aluminium: Why Search for new Production Routes?

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Observação

O fato deste trabalho estar escrito em Inglês, não se prende a nenhum pedantismo por parte do autor: a verdade é que, originalmente a intenção foi a de apresentá-lo nos E.U.A., onde a celeunia sobre o uso de novas fontes de Alumínio, vez ou outra, ressurge.

Entretanto, dado ao interesse do mesmo para o público brasileiro, resolveu o autor submetê-lo neste IV ENCONTRO NACIONAL DE TRATAMENTO DE MINÉRIOS.

Mister se faz acrescentar, não estar o autor fazendo apologias de métodos alternativos ao clássico H-H para a produção de Al primário. Longe disto, comercialmente, é o H-H o único viável, até o presente: mormente onde a energia elétrica e soda são disponíveis a preços competitivos.

O objetivo deste trabalho, portanto, é, além de efetuar uma revisão dos processos propostos, o de salientar rumos que se deverão ter em mente, na busca da melhoria ou substituição daquele processo clássico de obtenção do Al.

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1. Introduction

Minerals and fuels play a decisive role in economic growth, as well as in economic and military security. Therefore, the extent of their resources is a matter of vital concern to government and private enterprises.

The realm of most industry's concern over the extent of mineral resources is on the magnitude of the supplies that exist now or that can be developed in the near term. Of course, this is a matter of public interest, also.

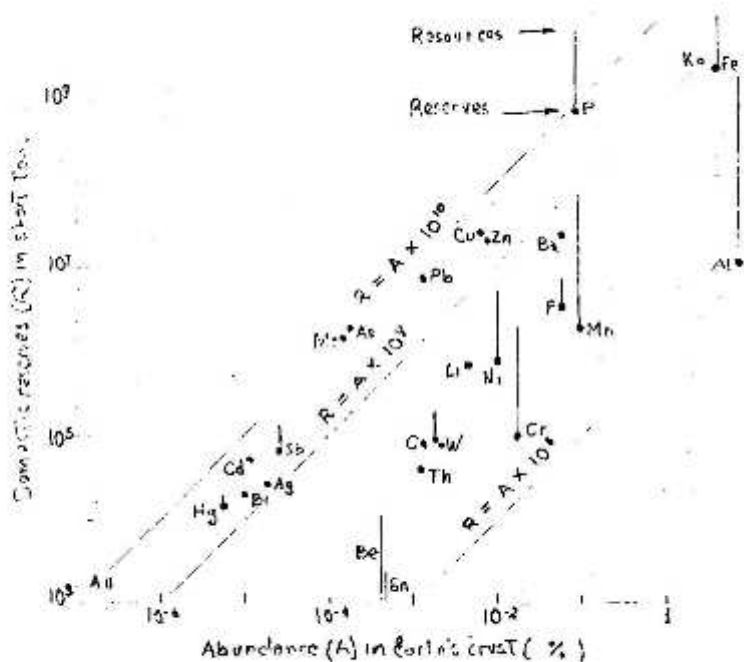
However, seems that the awareness of the "potential supplies" concept, a question that to be answered properly must take account both of the extent of undiscovered deposits, as well as deposits that cannot be produced profitably now, but may become workable in the future (see as an example the taconite deposits), is becoming more and more widespread among government officials and enterprises executives.

It is a well established fact, nowadays, that the quantity of usable resources is not fixed but changes with progress in science, technology and with variations in economic and strategic conditions.

As presented by McKELVEY (1), resources may be grouped into three broad categories: recoverable, i. e., the actual reserves, paramarginal, and submarginal. Paramarginal resources being defined as those recoverable as prices as much as 1.5 times those prevailing now. Deposits of this category thus become available, in commercial terms, at prices increases that can be borne without serious economic effects, and chances are that improvements in existing technology will make them available at as prices little or no higher than those prevailing now.

It is interesting to note that many of the fuels and minerals being processed today would once have been classed as submarginal, i. e., those for which no technology has been devised up to the point of their use, or too costly to be profitable.

A very good illustration of what has just been said is given by Figure 1(1), which shows the Abundance in Earth crust (%) versus U.S. reserves, in short tons of various elements.



The relationship shown above, of course, is only an approximate one, although very useful in order-of-magnitude estimates. A similar general correlation exists between Abundance of the elements and the number of minerals in which they are a significant constituent (1).

2. Which Factors Determine The Cut-Off-Grade, Workable Limits of Ore and Completeness of Extraction (2)?

Other things being equal, the lower the grade or the poorer the quality of the ore, the higher will be the cost of recovery of the valuable products. To the extent that there is a choice of the grade of the ore to be mined, there is also a choice of the total tonnage and of the total product recovered; the lower the permissible grade, the higher the tonnage. Therefore, the fixing of the cutoff grade in deposits of irregular grade-distribution may require several computations of alternative tonnages and grades on the basis of different assumptions as to mineable limits.

Equally important with grade is the workability of the ore which is measured by the cost of physical removal of the rock. Other factors, such as accessibility from mine openings, thickness and regularity of the ore zone, hardness and toughness of the ore, presence of interfering structures, such as faults, weak ground, et alia; all must be evaluated when the decision on which ore must be taken should be made.

Variations in the grade in the workability of an ore body, may go side-by-side, or they may partly compensate each other. Ores of many different grades and many different costs, but sufficiently similar in other qualities to be amenable to the same treatment process may be mined or blended to profitable recovery of otherwise paramarginal ore.

Complete removal of all available ore from mine, or complete extraction of all valuable products from the mined ore is never achieved. Cost per unit recovered rise almost continuously and usually with increasing steepness as attempts are made to increase the percent extracted. In the short run, with the recovery plant given, the percent extraction of metal will depend, to some extent on the grade of the ore itself.

Another important point is that the mining method usually limits the recovery of the ore in the mine.

3 — Which Factors Affects the Economics of Paramarginal and Submarginal Resources?

Finding, production, transportation, recycling and external costs of producing primary raw material are the major items determining whether a paramarginal or submarginal resource may emerge to the reserve category.

Finding costs are increasing and will do so in the future. New finds involve expensive techniques and the rate of findings by these techniques has been substantially lower than that of the past.

Production costs are, also, rising for many minerals; for some metals a century of decreasing cost appears to be over (3). New technologies, of course, can lower those costs, allowing more materials available from known deposits at lower cost. However, the fact still remains that known deposits are finite and their exploration under any technology involves increasing costs, as quantities increase.

Transportation costs also tend to increase on a world wide basis over time; the new deposits tend to be more remote from market places as times goes on. This is a tendency which can be offset, partly, by improved technology in transportation and, on the other hand, by bringing some paramarginal deposits into use.

External costs are those which have not played their role in the past, but which today are playing an important share in the cost structure. They usually take the form of regulations prohibiting certain mining operations in certain areas and delineating environmental protection procedures for the utilization of raw materials.

The main point of all this discussion is, simply, to indicate that **minerals from new deposits are likely to increase substantially in cost** over the next decades.

In contrast (4), the cost of recycling new minerals bears a good hope of reduction, due to the following facts:

- the stock of recyclable materials is becoming larger and larger, with the concentrations of the materials becoming more economic to utilize.
- they exist where consumption exists. Therefore their utilization brings an almost zero cost of transportation.
- they share already substantial external costs
- research has been very active to create new technologies for these materials.

5 — What is the Place of Aluminium in All This?

Aluminium is one of the most abundant elements on Earth. Its production, in the metallic form, is solely dependent on Alumina* coming from Bauxite deposits.

Bauxite reserves are large and no long run shortage of this commodity is anticipated (5). However, due to national security reasons, such as a desire for less dependability on foreign raw materials, and because of large quantities of paramarginal and submarginal reserves of Al in the U.S.A., new processes for extracting Alumina from non-bauxite ores are being sought.

In a Report of the National Materials Advisory Board (6) the various processes of obtaining Alumina from sources other than the conventional one have been described and evaluated. The Report concludes recommending further development work on HCl and HNO₃ processes for producing Alumina from clay.

In a more recent publication (7), the U.S.B.M. revised and updated cost estimates for producing Alumina from domestic raw material

Notwithstanding, the overall problem is not just of a metallurgical nature one, as might be apprehended from the previous discussion on resources, cut-off-grade, workability limits, and etc...

6 — Therefore, What is the Real Problem of Aluminium?

From the analysis carried out in the preceding paragraphs, one may see that resources are "living things": they exist, they become, they are used up and abandoned and, sometimes, retaken again.

All this will depend, mainly, on economical as well psycho-social pressures — such as strategy — which in turn, will force technological innovations.

Thus, seems to me, that, from a purely technical focus, the real efforts in getting higher returns on the production of Aluminium will come, not on the worrying about getting Alumina from non-bauxite ores, but, mainly, on searching for better methods of Alumina reduction, than the classical Hall-Heroult process.

Lets clarify this point further.

The following diagram shows a typical mass balance for the conventional Al production (Bayer + Hall-Heroult process).

From the diagram, one readily visualize the energy expenditures of the overall process.

Of the total energy, required to produce Al metal, 82% of it goes to the Hall — Heroult cell, which, besides, consumes also, six other highly valuable materials.

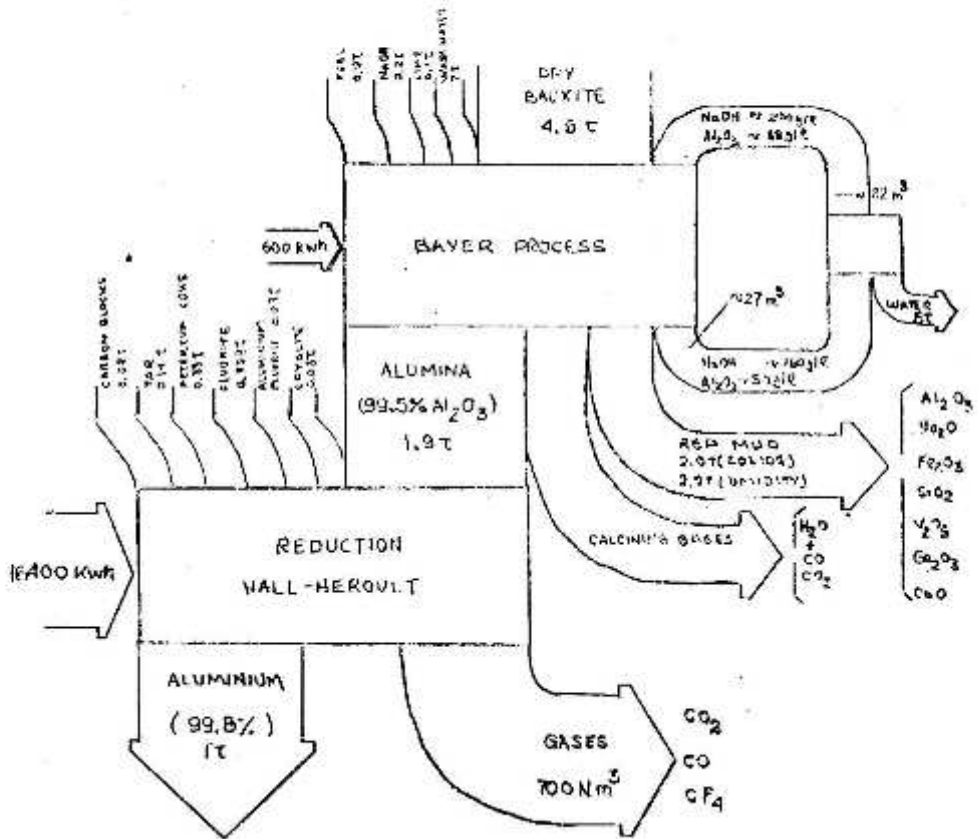
Therefore, taking aside non-technical factors, it is on the Hall — Heroult cell that relies the very answer of Aluminium production improvements.

7 — You May Say, All This is Fine, But What About Non-Technical Factors?

These, of course, are hard to estimate. They will depend upon so many aspects, some very contradictory ones, that just guesses can be made.

* Aluminium production exists, also, from Alunite (K₂SO₄. Al₂(SO₄)₃. 4Al(OH)₃, in U.S.S.R. (8).

MASS BALANCE TO PRODUCE 1 MTON OF Al
(BAYER + HALL HEROULT PROCESS)



REFERENCIAS MACHADO (3)

SEVRYUKOV (8)

VERSIANI DOS ANJOS (10)

It is true, nevertheless, that following the example of the successful organization of petroleum exporting countries, Jamaica, Australia, Guyana, Surinam, Sierra Leone, and Yugoslavia formed the International Bauxite Association.

As put by BLUMENREICH (12): "The immediate effect of these actions was to raise the cost of aluminum substantially, increase the U.S. balance of payments deficit in aluminum, make the recovery of aluminum from domestic aluminous raw materials more attractive, and weaken the reliability of traditional suppliers of aluminum raw material. To alleviate this situation, the U.S. Bureau of Mines and private industry are engaged in cooperative program to test the extraction processes for domestic aluminous materials... High alumina clays, androthosite, and alunite-considered the leasing potential sources of aluminum — are readily available in the U.S."

However, energy continued to occupy a "primus inter pares" position among the problems facing the aluminium industry.

Paradoxically enough, the necessity of energy conservations has spurred growth opportunities for aluminium (12), particularly in automobiles for light weight and gasoline conservation; in housing for insulation and heat reflectivity; in light weight cans to reduce transportation costs, and etc...

Therefore, the need for aluminium is raising.

D.P. REYNOLDS addressing, as the chairman of the Aluminum Association, established, as the objectives for the industry: to conserve capital, bauxite, energy and to reduce pollution.

As a practical matter he proposed to increase the recovery of recycled aluminium by 1977 to 1 billion pounds; each pound of metal thus obtained saves 95% of the energy required to extract aluminium from virgin materials.

All this bring us back to the point discussed earlier — under the headline: Which Factors Determine Cut-Of-Grade... —, as well as to the 82% energy expenditures in the Hall — Heroult cell. Moreover, continuing inflation is affecting aluminium costs in several ways. A recent increase of 27% in electric power rates was put into effect in the Pacific Northwest; also increases in gas fuel prices and coal are turning cost of power tremendously high in most of the plants.

This is not the full story as yet: the unusual economic conditions of the 74 year, moved up expenditures in raw material to a parallel position to those in energy (12)

This reminds me of a speech delivered by AGARWAL — director of research of the Ledgemont Laboratories — in a informal seminar held at Columbia University, last year, when he told the attendants that he firmly believed that for the first time in history, the copper prices will show a reserve trend compared to those of aluminium.

8 — Thus, Concluding

KELLO, Professor at Columbia, in the very same seminar referred as above, and later, in a article (13), summarised the energy problem by saying: "Growing scarcity and rising prices of fuels, electric power and some raw materials are likely to play havoc with conventional practices in our mineral and metal producing industries for many years to come... the following features of this near-future period appear inevitable:

1. Energy prices will be erratic and much higher than those to which we have become accustomed.

2. Industry may find it necessary to change from one fuel to another, or from fuel to electric power (or visa-versa, in some cases), as dictated by prices, local supply and by changes in our overall energy supply pattern.

3. Finally, and this serves as the theme of this paper, our processes industries will spend much time and money on a neglected aspect of their business — how to improve the energy efficiency of their process".

The above quotation brings to our mind a reflection; methods of getting alumina from non-bauxite ores are fine, but their economies can't beat, at the present moment, as well as in the nearby future, that of the Bayer process. This is mainly so because of the enormous control of the economics of these non — bauxite ores exercised... the bauxite producing countries!

A price alleviation in bauxite and....

Besides, the critical point of producing aluminium is the Hall — Heroult process, in terms of energy consumption, and all these proposed methods of getting alumina from non-bauxite ores will ask, at least today, for the H-H process.

Thus, again, it seems to me much more logical to expend efforts, in either optimizing the H-H process or to develop alternative and competitive processes to the H-H cell.

11 — Getting Aluminium from Process Other Than Hall — Heroult

Many improvements on the H-H process have been reported in the technical literature. Improvements on building and operation of the cells (14), (15), (16), on new cell models

(17), (18), on process control (19), (20), (21), on the fundamental aspects of the cell reaction (22), (23), (24), (25), on the power consumption (26), on electrolyte composition (27), (28), (29), and others.

However, despite all these studies and improvements the process still lacks, in energy efficiency, as report before, needs capital intensiveness, and operates in very large scale.

Environmental considerations, also, plays a very important role in the seeking of new methods of production, as pollution control of existing facilities is difficult and expensive.

Much research effort has been spent in finding a suitable substitute for the H-H process, or for the overall Bayer H-H process; but as yet, none of these lab bench and pilot-plant processes have reached commercial production. Chlorination being the magic word in all of the most promising reduction processes.

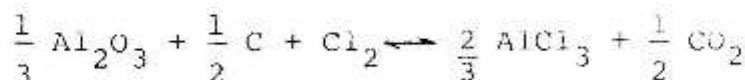
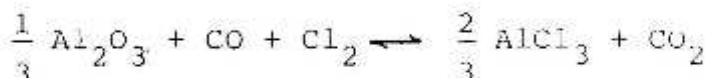
Therefore, before going into the description and analysis of these various processes, lets have a look on the chlorination of aluminium bearing ores and its possibilities.

The Ellingham diagram presented as follows was drawn based on data given by OTHMER, NOVAK and DURAK (30). It shows the Gibbs Free Energies of direct chlorination and reduction-chlorination of the metal oxides which are of interest to the production process of aluminium.

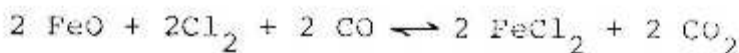
For the purpose of cleareness not all the possible chemical reactions that may occur were presented.

The following equations may also occur:

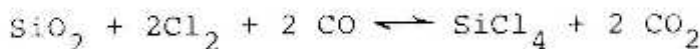
1 . ALUMINIUM



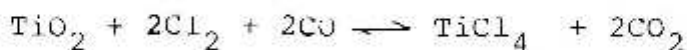
2. IRON



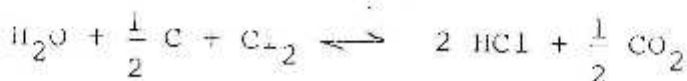
3. SILICON



4. TITANIUM



5. HYDROGEN



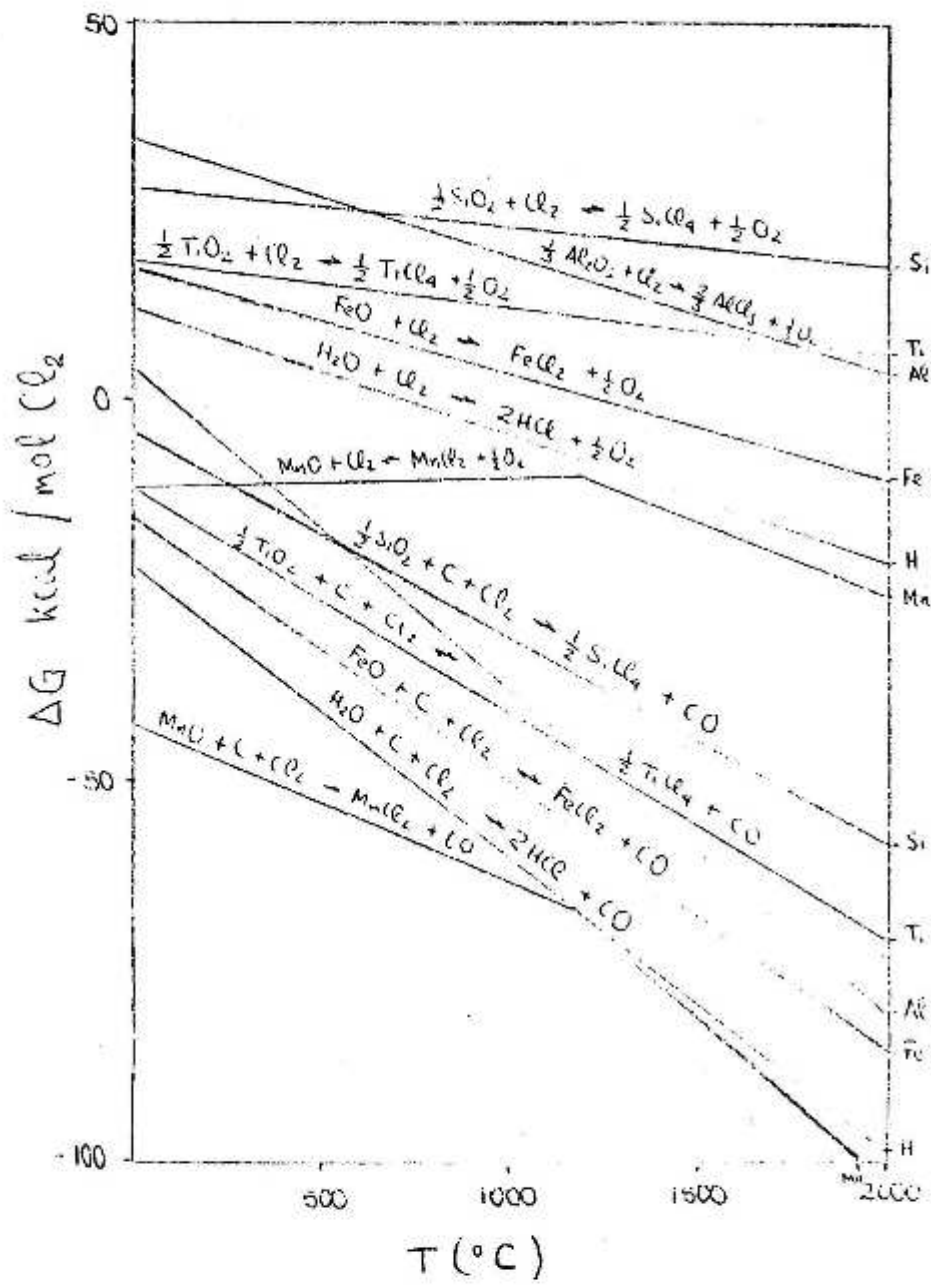
6. MANGANESE



From the Free Energy diagram given in the following page, it may be seen that while direct chlorination of the metal oxides presents positive free-energies, except at very high temperatures for Fe, H, and Mn. reduction — chlorination makes the decomposition of the oxides feasible.

Four processes, all of them based on the decomposition of Aluminium Trichloride, have been developed and are claiming significant advantages over the Bayer-Hall-heroult process. They are the ALCOA, ALCAN, TOTH, and MONOCHLORIDE, with the first two of these tested on a pilot-plant scale.

A fifth process, based on the extraction of aluminium from Al-Si alloys by its electrolysis in molten electrolytes has been tested, on lab scale, by the U.S. Bureau of Mines.



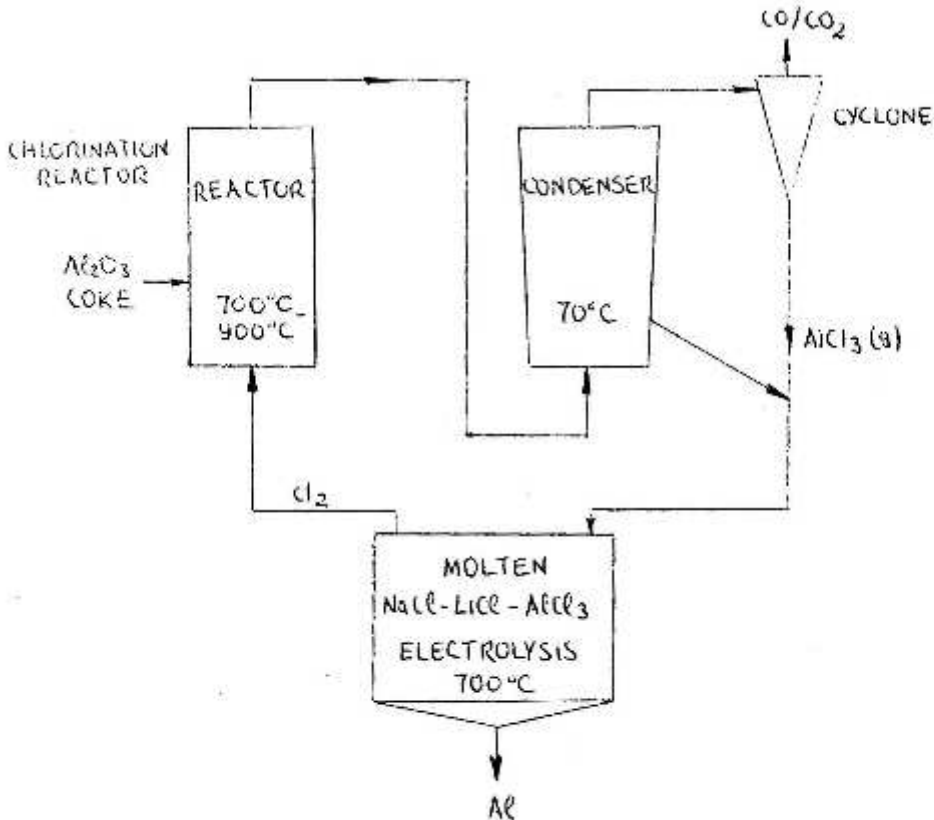
ELLINGHAM DIAGRAM - Cl

ALCOA SMELTING PROCESS

ALCOA have expended \$ 25 million over 15 years of research. A 15,000 ton per year pilot — plant has been reported under construction (31)

Details of the process are scarce, but a probable flowsheet has been published by PEACEY and DAVENPORT (32)

The figure below illustrates the ALCOA Process



ALCOA SMELTING PROCESS

Stages:

— Bayer alumina is reduction — chlorinated at 700°C — 900°C , producing a vapour mixture of AlCl_3 , CO and CO_2 .

— AlCl_3 is condensed at about 70°C , in a fluidized bed consisting of solid AlCl_3 particles.

— Solid AlCl_3 is, thus, fed continuously into an electrolytic cell, containing a fused salt chloride electrolyte, consisting of:

50% NaCl
45% LiCl
5% AlCl_3
at 700°C .

— Liquid aluminium metal is produced, applying d.c. current to the terminals of the electro-winning cell, and gaseous chlorine is, thus, evolved at the anode.

— Chlorine thus formed is recycled to the chlorination stage.
Two cell designs have been reported by ALCOA (32):

— a monopolar cell, similar to the H-H cell, operated at 3.3 V and $13,000 \text{ A/m}^2$, with a power consumption of 11,500 Kwh/metric ton of aluminium, having a current efficiency of 86%.

— a bipolar cell, containing four bipolar electrodes, consisting of a horizontal anode at the top, a horizontal cathode at the bottom, and a bipolar electrodes in between.

The novel feature of this bipolar cell is that each bipolar electrode behaves as a cathode on its top surface and as an anode on its bottom surface. This cell, is equivalent to five monopolar ones in series, has a cell voltage and productivity approximately five times that of a convectional H-H cell, operating at the same current — density.

Both cell arrangements are claimed to reduce power consumption over the H-H cells, due to the higher electrical conductivity of the electrolyte ($40 \text{ ohm}^{-1} \text{ cm}^{-1}$ against $2.8 \text{ ohm}^{-1} \text{ cm}^{-1}$ for cryolite at 950°C), and the smaller interpolar separation.

It has been claimed, also that the ALCOA process will lower electrical energy requirements by as much as 30% over the most efficient conventional practice, occupying a much smaller plant area.

ALCAN PROCESS (32), (33)

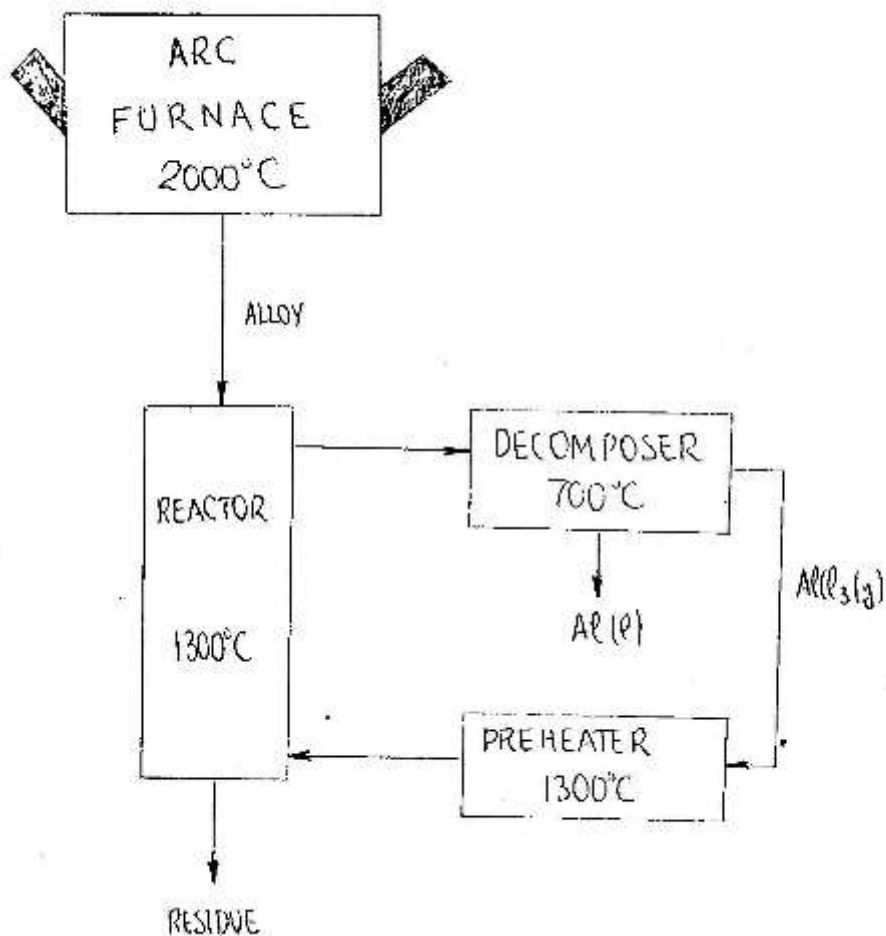
Forty million dollars have been expended, over a 12 year period, in the development and building of a 5,000 ton per year pilot — plant. This plant was shut down due to stress corrosion problems. Although, ALCAN reports the solving of these problems, no further pilot — plant work has been carried out since seven years ago.

Next page is shown a flowsheet illustration of the main aspects of the ALCAN PROCESS.

The main features of the flowsheet shown are:

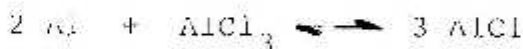
— Bauxite and coke are smelted in an open electric arc-furnace, at about 2000°C , producing a crude alloy containing:

50% wt Al
30% wt Fe
10% wt Si
5% wt Ti
5% wt C



ALCAN PROCESS FLOWSHEET

— The alloy is thus reacted with preheated $AlCl_3$ vapour, at $1300^\circ C$, in the converter. Near 50% of the $AlCl_3$ reacts with metallic aluminium in the alloy, yielding Aluminium Monochloride vapour, according to the reaction:

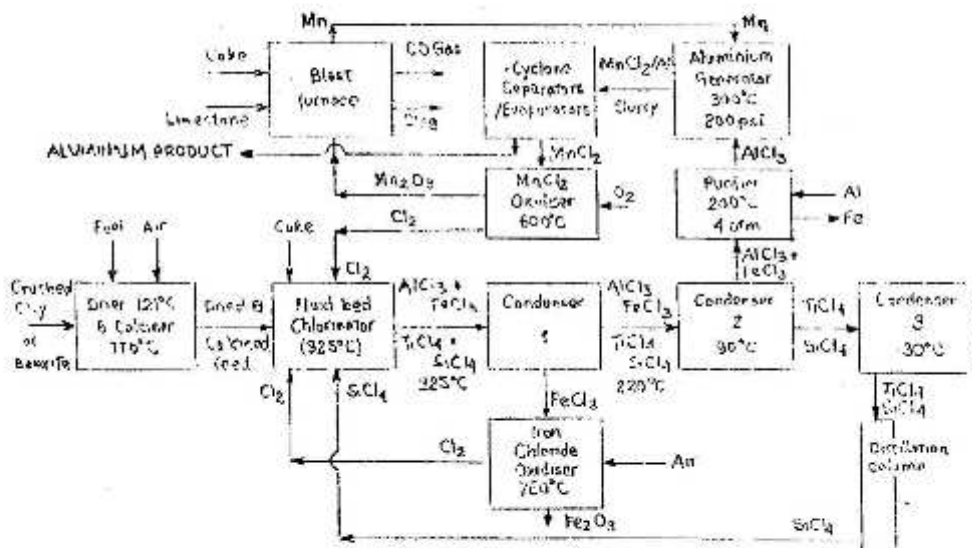


— The chloride vapours are directed to the decomposer, being cooled to $700^\circ C$ in a stream of molten aluminium droplets. This stage allows the decomposition of the $AlCl$ to metallic Al and the original $AlCl_3$ which is recycled.

Capital investment reduction of 50%, lower operating costs and economical operation on a smaller scale, all this, have been claimed by ALCAN.

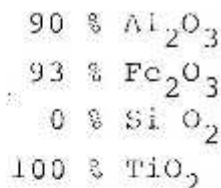
TOTH PROCESS

Applied Aluminium Research Corporation, A.A.R.C., an American based company, is trying to raise about \$ 30 million to finance pilot - plant work, to test this process. The following flowsheet illustrates the TOTH PROCESS.

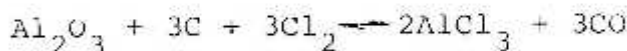


The basic points of the process are (34):

— Reduction — chlorination of calcined raw material (any aluminium containing material), producing $AlCl_3$ vapours which are purified. The addition of $SiCl_4$ to the reactor is performed in order to suppress the chlorination of SiO_2 . The extent of chlorination is estimated at:



— Then main reaction at this stage is:



— Liquid $AlCl_3$ is reacted with solid Mn metal to form $MnCl_2$, at 300 C, and 200 psi, according to the reaction:



— MnCl_2 is oxidized to MnO and the chlorine is recycled to the chlorination stage, according to:



— Manganese oxide is, thus, carbothermally reduced to metallic manganese, and the latter, is recycled:



The replacement of electrical reduction by the carbothermic reduction to produce aluminium, as well as the direct use of widely distributed Al bearing materials, has been claimed as one of the big strikes of this process.

Mr. TOTH claims that the cost of building a plant could be reduced by somewhere between 50% and 75%; the production cost reduced by 50%; that there could be a reduction in the consumption of electrical power of 90%; and that pollution problems associated with the conventional Bayer — Hall — Heroult process would be eliminated.

However, various questions are pending:

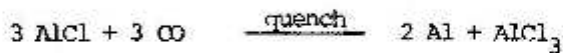
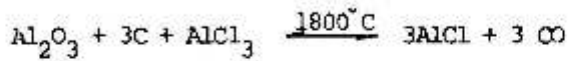
— The use of Mn metal as reductant does not appear to be economically feasible (31). From the stoichiometry of the reaction, at least 3 tons of Mn must be used for every ton of Al produced. Therefore, Mn hold-ups are likely to occur; also, the regeneration of Mn in a blast furnace is likely to be expensive (calculated figures (32) giving about 5 tons of coke per ton of Al produced), besides the formation of Mn_7C_3 (35), which has a limited efficiency in reducing AlCl_3 .

— The energy savings claimed are open to contestation, for Al_2O_3 standing towards the lower part of the Ellingham diagram, will require large energy inputs, no matter the route taken.

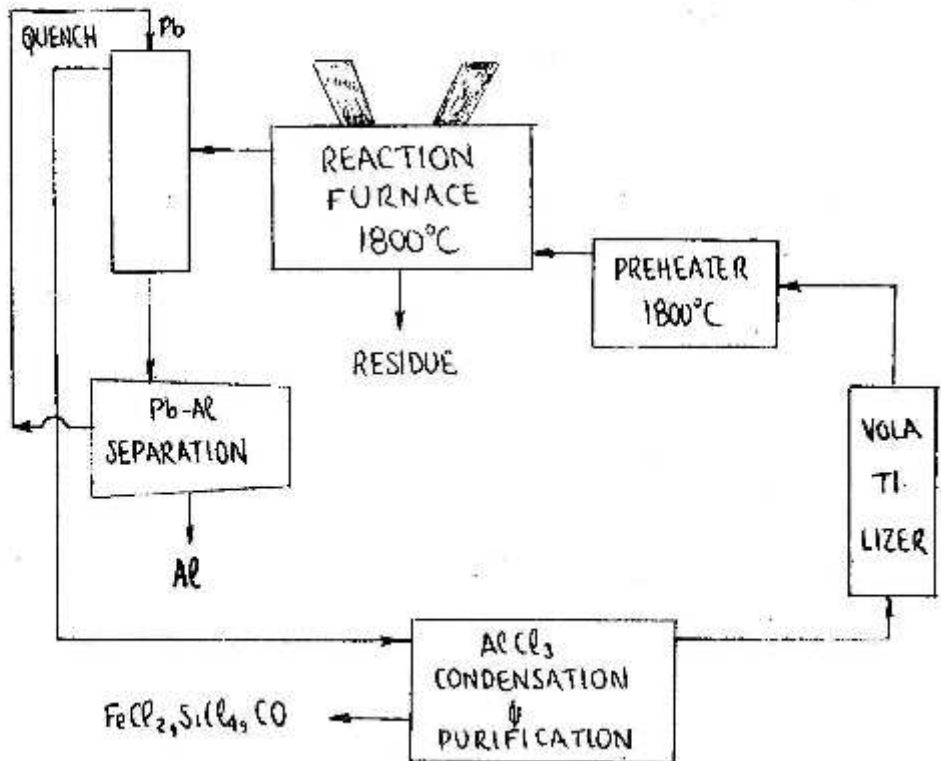
— The use of fluid bed chlorinators, and chlorine vapours in the process streams might led problems of pollution control and corrosion.

MONOCHLORIDE PROCESS

Demonstrated on a laboratory scale, actually constituting a PhD thesis at the U. of Leeds, England, this process produces aluminium, containing Si inclusions, directly from Bauxite through the carbothermic formation of Aluminium Monochlorite, according to the reaction:



The basic features of this process are shown below .



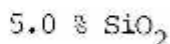
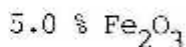
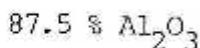
MONOCHLORIDE

Stages:

- Preheated AlCl₃ passed through a bed calcined bauxite and coke, at 1800 C, in a high temperature reactor.
- AlCl, CO and some SiCl₂ and FeCl₂ thus formed are passed into a decomposer.
- At the decomposer, molten Pb, at 700 C, is sprayed into the hot gases, allowing the desproportionation of AlCl and SiCl₂ to form Al, Si, and AlCl₃ and SiCl₄.
- The Pb alloy obtained from the decomposer is slowly cooled to 700 C in the separation unit.

— Molten Al, containing small amounts of Pb and Si would float on top the Pb and is tapped. $AlCl_3$ is separated from the gases leaving the decomposer and recycled to the main reaction unit.

A final alloy containing less than 1% wt Si is claimed to be produced from a calcinated Bauxite having the following composition:



Also, has been claimed that the process, consisting of a continuous closed circuit, is able to operate economically on a small scale, reducing capital and operating costs (36)

U.S.B.M. — Al-Si ALLOY PROCESS

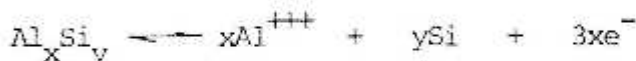
As a mean of utilizing domestic aluminium silicate ores for the production of metallic aluminium, the USBM investigated (37) the extraction of Al from Al - Si alloys by electrolysis in molten electrolytes of $NaCl - KCl - AlCl_3$ and $NaCl - KCl - AFL_3$ in a laboratory scale.

The test runs were carried out utilizing six different alloys, with Al contents varying from 20% to 87%, producing Al products of primary grade or better. More than 80% of the Al was claimed to be recovered with current-efficiencies as high as 91%, as well as the recovery of a metallurgical-grade Si product from the anode residue, when employing the 50 - 50 and 65 - 35 Al - Si alloys.

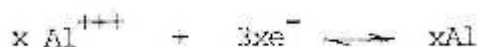
It is also claimed that the electrolytic step requires a lower temperature for operation than the H-H process, eliminates the preparation of alumina, employs less costly electrolytes, and consumes no carbon for the removal of oxygen.

The reactions taking place during the electrolysis of the Al-Si alloys are as follows (37):

AT THE ANODE



AT THE CATHODE



OVERALL REACTION



where x and y represent the proportion of Al and Si in various alloy compositions. No economical data has been presented.

12 — Comparing The Various Processes (32)

Although the limitations of the accuracy of the presented data has been recognized, the following table compares estimates of the probable capital and operating costs, electric power and carbon requirements of the ALCOA, ALCAN, TOTH, and MONOCHLORIDE Processes, with the best available BAYER — HALL — HEROULT Process Technology.

Process Evaluation and Comparison with the Best BAYER-HALL-HEROULT Technology (Scale 1:10000 M. Tons/Year)

	BAYER-H-H	ALCOA*	ALCAN	MONO*	TOTH
Fixed Capital Invest. (\$ per Annual M. Ton of Al)	1700	-5%	-45%	-40%	-40%
Direct Operating Costs (\$ per M. Ton of Al)	350	+10%	0	-15%	+50%
Electrical Energy (kWh per M. Ton of Al)	14000	-20%	+80%	+5%	-85%
Carbon Requirement (kg per M. Ton of Al)	450	-20%	+120%	+70%	+1000%

* Bipolar Cell, includes cost of Bayer Plant

* Bauxite Starting Material

From the figures presented in the table, one might conclude:

— The ALCAN process shows higher power requirements, although reduces carbon requirements.

— The TOTH process requires the highest operating costs and carbon consumption of all proposed processes. However, it reports a cut in electrical energy requirements by 85% of the original Bayer — Hall — Heroult cell.

— The MONOCHLORIDE process offers the largest reduction in direct operating costs, as well as shows a decrease in 40% for fixed capital investment (comparable to the ALCOA and TOTH processes).

— The ALCOA process gives large power savings and offers significant reduction in capital and operating costs. Research has been active and seems to be the most promising of all processes (32). (38).

13 — Research Work on Aluminium Chloride Processes

A good of research work has been conducted in aluminium chloride processes. The condensation of $AlCl_3$ vapour has been studied by COOKSTON and NANWAY (39), and by JORGENSEN (40); the kinetics of $AlCl_3/AlCl$ reactions by KIKUCHI (41); the effect of

impurities by FOLEY and Moyle (42), the cell design and operational parameters by DENHOLM (43), KIRKY (44), SIGLETON (54) and SLATIN (46).

A comprehensive review of the physical chemistry of Aluminium Chloride vapour reactions has been given by GROSS (47).

14 — The Secondary Aluminium Industry

Following Mr. REYNOLDS recommendation, it doesn't seem to be reasonable ending up this paper without giving same consideration to the secondary aluminium industry.

Secondary smelters provide the needs of the casting industry (48), (49). Recycling scrap is the raw material of this segment of the industry, which produces about 1,200,000 ton per year. (12).

Magnesium is the chief impurity to be treated, since it affects ductility and volumetric growth, resulting from the precipitation of magnesium silicide with aging, at room temperature (50). However, most of the raw materials for the secondary smelter came from the mill products of the primary aluminium industry that are high in Mg concentrations (51).

The Mg content a normal bath is about 0,5% to 0,8% Mg, which must be turned down to a value less than 0.1%.

Due to the higher free energy of formation for $MgCl_2$ compared to $AlCl_3$ (52), a process known as "demagging", involving halogenation of the Al-alloys, is commercially utilized.

Pollution problems, however, resulting from the effluents containing deleterious halogen compounds, have forced the shut down of some of the secondary plants.

ALCOA (53) developed a reaction chamber, divided in various compartments, through which molten Al flows. Chlorine is introduced through a reactor that disperses the gas in tiny bubbles. Efficiencies of 100% Cl_2 utilization have been reported (50).

Another approach is the DERHAM Process (54) in which Cl_2 gas is injected at a submerged stream of molten Al-alloy. Intimate contact of the reactants is provided by a specially designed discharge spout.

Important aspects of the secondary Al industry are:

- the variety and quality of the alloys (55)
- the preparation of charge for smelting (55)
- the pollution problem. (50)

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