

***"Materials-Cycle Optimisation in the
Production of Major Finished Materials"***
**CHAPTER 2: ALUMINA, ALUMINIUM
AND GALLIUM**

by

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This chapter is part of a report made for the EC DGXII on a project entitled **"Materials-Cycle Optimisation in the Production of Major Finished Materials"**. This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
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- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
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- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

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CHAPTER 2. ALUMINA, ALUMINUM AND GALLIUM¹

2.1. Summary

Aluminum is an industrially important metal that plays an extremely important part in modern society. Without it there would be no aircraft industry, for instance. It is light, corrosion resistant, and easy to bend, draw, extrude, stamp and form into shapes. It is highly reflective. It is a good thermal and electrical conductor. It is also very easily recycled. There are virtually no environmental problems associated with its use or disposal.

However, the extraction and refining of aluminum are less benign. The mining of bauxite is environmentally destructive, for one thing. Bauxite is obtained from open pit mines, from which overburden has been removed, using draglines. The layer of ore is usually rather thin. It follows that relatively large amounts of material are removed in relation to the amount of ore recovered. Some companies have restored former bauxite mines in exemplary fashion, even receiving UN awards. However, regulation tends to be weak or unenforced in many of the less-developed countries where bauxite is mined. Given the mixed record, bauxite mining has been strongly opposed by local residents in some areas (e.g. India).

The processing of bauxite to alumina generates large quantities of caustic waste, called "red mud" which has proved hard to dispose of, or to utilize. Furthermore, aluminum metal smelting is extremely energy intensive. For this reason alternative processes for extracting aluminum, from different sources and by different technical means, should be considered seriously, even though aluminum and its major source (bauxite) are hardly scarce.

Aluminum has been called "congealed electricity" because so much electric power is consumed in its production. The energy required to manufacture four aluminum soft drink or beer cans would be equivalent to the energy content of one of those cans filled with motor gasoline. Because of its high energy-intensity, aluminum companies have located smelters mainly in areas where long-term contracts for cheap electricity could be obtained — generally at or near the sites of new dams in remote locations. The industry points out that in many cases the aluminum industry provides a reliable base-load without which the hydroelectric project could not have been justified in the first place.

But, while this is true, it is hardly a sufficient justification for very long-term contracts at extremely concessionary prices. Many third-world politicians are willing to negotiate such contracts in exchange for immediate benefits to themselves, but at the expense of future generations of their own people. Meanwhile, the aluminum companies and their customers from the industrialized world benefit from unreasonably low prices, which also encourages frivolous uses (such as beer cans) — together with wasted energy — and discourages technological innovation in the industry. For these reasons, metallic aluminum should not be used in ways that lead to dissipative losses, especially in packaging. To the extent that it is used for beverage cans, it should be recycled far more intensively than it is at present. Recycling requires only about 5-7% of the energy needed for producing virgin aluminum. In fact, the low rate of recycling of aluminum cans in Europe — much lower than in the U.S. — is extremely wasteful (see *Chapter 11, Packaging*).

Aluminum smelting is also responsible for significant problems of atmospheric fluorine pollution. While largely controllable, it is nevertheless a hazard, especially to workers and local residents if the technology (and its maintenance) are not of the highest standard.

Gallium is a metal that has found economic uses only in recent years, partly because it is never found in pure form or in high quality ores. It is currently recovered as a by-product of aluminum refining. Gallium is a "transition metal" of considerable potential importance because of possible future increases in demand for gallium arsenide and other semiconductors.

Goals of Public Policy: Reduce environmental damage due to surface mining; reduce generation of wastes (red mud) from Bayer process; reduce electric power consumption; reduce dependency on petroleum coke; reduce fluoride emissions; increase recycling of aluminum (especially cans) in Europe.

2.2. Aluminum, Electricity and Developing Countries

Aluminum companies argue that they should not be charged with wasting energy on the grounds that most aluminum is smelted with cheap coal or hydroelectric power from remote places where other uses for that energy have not developed. Aluminum companies have even argued that the energy intensiveness of aluminum is an advantage, as an added incentive to develop such energy resources. However, even where "cheap" energy resources are used, as in Australia, Canada, Brazil, Ghana, Iceland (and formerly in France, Norway, Switzerland and the U.S.) the argument is often deceptive.

In the first place, the long term contracts that attract aluminum companies are typically much longer than the "development" argument would justify. In the second place, electric power, regardless of source, is potentially fungible, even though there may be no way to transport the power at the moment the aluminum smelter is first built in a remote place. It can also be transported for very long distances, overland or even under water, by using extremely high voltages, up to 1 million volts. Third, if the local electricity supply is limited by prior appropriation, other kinds of industrialization may be inhibited. (In effect, hydroelectric power now used to smelt aluminum could — in many cases — just as well be diverted to other social purposes, creating more jobs for local people.

The aluminum industry has unquestionably promoted hydroelectric (and nuclear) power development. It has not simply followed hydroelectric development that would have occurred anyway. On the contrary, new hydroelectric facilities are often built — as in Brazil, Ghana and Venezuela — with the explicit intention of attracting aluminum smelter investments to follow. The argument is that aluminum smelters provide hydroelectric power suppliers with a predictable "base load" thus making it possible to exploit power sources that might not otherwise be economical, and facilitating other economic development. For example, Venezuela apparently saw hydropower development as a way of diversifying its energy base away from oil [Altenpohl 1982 p.9].

The other side of the coin is that some extremely questionable hydro-electric dam projects have been built, largely for aluminum companies, in a number of remote areas, flooding and otherwise damaging huge areas of virgin forest and tundra, largely for the special benefit of the aluminum industry. A few examples are worth citing [Young 1992]:

- (i). The Akosombo dam on the Volta River in Ghana sells three quarters of its power to an aluminum smelter, at extremely low prices (the world's lowest in the early 1980's); it has done so by flooding 5% of the land area of the country, and accelerated coastal erosion by interfering with the movement of sediments to the Volta estuary. Ghana has received virtually no collateral benefits from the project, not even promised irrigation. It has lost arable land, thanks to the Akosombo project.
- (ii). The Tucuruí dam on the Tocantins River, a tributary of the Amazon, is part of the infamous Carajas Project in Brazil, partially financed by the World Bank. The dam sends one third of its output, at subsidized prices, to aluminum smelters. The artificial lake behind the dam flooded six towns and two Indian reservations. It left at least 20,000 people homeless. Another Indian Reservation was heavily damaged by the building of power lines and an electrified railroad to carry iron ore (to a blast furnace fueled by wood!) A Brazilian government report estimated that subsidies account for 60% of the value of exported aluminum.
- (iii). The James Bay project of the utility Hydro Quebec has offered aluminum producers long-term contracts at 0.75 cents per kwh for the first five years and 1.5 cents/kwh thereafter. This project, when complete, will flood an area larger than Lake Erie. It is especially mysterious that the Quebec government should elect to provide heavy subsidies to aluminum smelters, given that all of the power could easily be sold (at market prices) to the power-hungry northeastern U.S. Each job "created" by these subsidies cost \$171,000 in lost revenue.

The nuclear power industry in Britain, France and Germany was also linked (in the 1960's and 70's) to expansion of the aluminum industry. Nuclear power plants could be justified more readily if there was a ready-made customer waiting [Kirchner 1988, cited by Young 1992]. When subsidies are withdrawn, the industry usually moves away. This happened in the U.S. when long-term contracts dating back to the 1930's for cheap power from the dams of the Tennessee Valley Authority (TVA) and the Bonneville Power Authority in the Pacific Northwest finally expired a few years ago. ALCOA moved its smelters to Brazil and Australia. In Europe, Alusuisse, which was unsubsidized, has closed all its smelters except one in Norway and one in Iceland, where cheap hydroelectric power is available.

ALCAN, the Canadian company, owned all of its hydroelectric power supply (until the James Bay project came along), either in British Columbia or Quebec. Since the plants were built before 1950 the power was being charged internally at the marginal cost of production. In 1983 this was only 0.3 cents (U.S.) per kwh, one sixth of the average cost to the world aluminum industry at the time [Brown 1983]. By contrast, the price of electricity to U.S. aluminum smelters was 2.6 cents/kwh and Japanese smelters were paying 6 cents/kwh. To be sure, there is some justification for a price differential since it costs more to service many small customers than one large one. However it is hard to believe that the cost differential is anywhere near as great as the price differential.

In summary, the aluminum industry typically secures long-term supply contracts at very low cost when newly available electricity supply exceeds local demand for electricity. Yet, in most cases, these long-term contracts continue long after the electric power surplus is exhausted. Then, either further economic development is inhibited, or new supply — at much higher cost — must be provided by government to replace that which is being used for aluminum production. In Europe, four of the five leading aluminum companies are heavily subsidized. (The exception is Norsk Hydro, which also owns its own power source). Pechiney, in France, receives electricity from the state-owned utility (EDF) at a rate of 1.5 cents/kwh, compared to other industrial users who pay 6 cents/kwh and residential users who pay 12 cents/kwh. Pechiney apparently gets its electric power at one half to one third the actual cost of generation [Nectoux 1991, cited by Young]. This electricity could obviously be sold elsewhere in Europe at market rates.

In short, while aluminum smelting operations might conceivably be the "leading edge" of economic development in some remote regions, in the long run aluminum smelting has been significantly subsidized by other electric power users who arrive on the scene later and are forced to pay higher prices than they should. This is especially true in Europe. Apart from this, there are significant environmental costs associated with extraction and refining primary aluminum. It is argued by the industry that the leading edge investor is entitled to whatever long term advantage it can negotiate. If markets were perfect, this argument would be conclusive. However, in practice, large multi-national firms often negotiate deals with political leaders of developing countries who are corrupt at worst and have very short time horizons at best. Politicians, elected or not, typically, care little for the interests of future generations.

There is a further downside to the aluminum industry's worldwide quest for cheap (often subsidized) electricity. The very success of this strategy in recent decades has inhibited the industry from investing in new and improved technologies. Indeed, despite its association with technologically advanced sectors such as aerospace, the aluminum industry is still largely locked in to the same technology (notwithstanding marginal improvements) that launched it into the twentieth century. True, this is not *per se* a proof of technological backwardness, if the original technology happens to be the best possible one. However, there is some evidence that better (and cheaper) technologies do exist, as we note later.

2.3. Alumina: Sources and Processes

Aluminum is very abundant. It constitute 8% of the earth's crust (compared to 27.7% for silicon and 5% for iron), but never occurs in pure form. The major commercial ore at present is bauxite, which is largely found in the tropics and relatively near the earth's surface. There are two types of bauxite, karstic and lateritic. The former contains mostly alumina monohydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and the latter contains mostly alumina trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). The lateritic type is the product of weathering under humid tropical conditions, which is why so many bauxite mines are located in the tropics.

Early in the 1970's several major bauxite producers, including Guyana, Surinam and Jamaica, began to nationalize bauxite mining properties. In 1974 the major producers formed a cartel, modelled on OPEC, called the International Bauxite Association (IBA) with headquarters in Kingston, Jamaica. Royalties were increased and bauxite production taxes were imposed by four countries (Jamaica, Haiti, the Dominican Republic and Surinam), providing 80% of U.S. bauxite imports. The prospect of a bauxite shortage, and higher prices, prompted the U.S. Congress to ask the Bureau of Mines to investigate alternative sources of aluminum could be extracted at moderate additional cost from aluminum-bearing minerals such as aluminum phosphate rock, alunite², anorthosite, dawsonite (in oil shale), kaolinite (clay), and nepheline³ [Patterson 1977]. A number of minerals and extraction processes were investigated under this program [USBuMines 1975; Peters & Johnson 1974]. However, the producer cartel collapsed and prices stabilized before any of the alternative processes were sufficiently developed to attract investment.⁴

The major producers are Australia, Guinea, Jamaica and Brazil, although there are 13 countries with annual production in excess of 1 million

metric tons, or MMT. Total world bauxite output in 1991 was 107.92 MMT, barely up from 1988, as shown in *Table 2.1*. Total world production of primary aluminum in 1991 was 19.575 MMT, as compared to 18.495 MMT in 1988.

The biggest producer of bauxite in western Europe is Greece (2.13 MMT in 1991), followed by France (193 kMT in 1991, down from 1.53 MMT in 1985). Total mine output of bauxite in Western Europe was 2.335 MMT in 1991. In eastern Europe, Hungary and Yugoslavia are also producers (2.037 MMT and 2.7 MMT, respectively). However, over two thirds of the bauxite consumed in western Europe is imported, either from Africa, South America or Australia.

Table 2.1. Production of bauxite, alumina & aluminum (kMT)

<i>Country</i>	<i>Bauxite 1991</i>	<i>Alumina 1991</i>	<i>Aluminum 1991</i>
Austria			80
France	193	150	286
Germany		1165	690
Greece		520	152
Iceland	2130		89
Ireland		900	
Italy		760	218
Netherlands	9		264
Norway			833
Spain		950	355
Sweden	3		97
Switzerland			66
United Kingdom		110	294
W. Europe	2335	4545	3414
Albania	8		
Czechoslovakia		150	68
Hungary	2204	546	64
Poland			45
Romania	200	400	158
Yugoslavia	2700	900	
E. Europe	5112	1996	315
Turkey	530	159	57
USSR	3800	3000	2400
USA	na	5230	4030
Australia	40503	11713	1235
World	107920	39827	19575
<i>Source: [USBuMines 1991, revised]</i>	<i>Table 35, p.224</i>	<i>Table 37, p.226</i>	<i>Table 20, p.215</i>

Table 2.2. Composition of some typical bauxites, by weight percent

Constituent	Jamaica	Surinam	Guinea	Arkansas	Oregon	Washington	Hawaii
Al ₂ O ₃	49.0	59.8	58.6	40-60	35.0	38.3	25.9
Trihydrate	47-50	59.6	52.7				
Monohydrate	2-9	0.2	5.9				
Fe ₂ O ₃	18.4	2.7	4.1	3- 6	31.5	28.7	39.4
SiO ₂	0.8	3.8	4.9	1-20	6.7	6.5	4.7
TiO ₂	2.4	2.4	2.5	1- 3	6.5	4.2	6.7
Other minor	0.7	0.1	0.02				
H ₂ O, combined	27.5	31.2	29.6				
Loss on ignition				15.35	20.2	21.7	20 - 26

Source: [Battelle 1975 Appendix B]

Bauxite is a mixture of aluminum oxide, Al₂O₃ (about 50%) and other oxides, notably Fe₂O₃, SiO₂, TiO₂ and combined water as shown in *Table 2.2*. It is first reduced to alumina trihydrate (Al₂O₃·3H₂O), or aluminum hydroxide (Al₂(OH)₃) by a chemical process of purification and separation, known generically as the Bayer process. The Bayer process starts with finely ground bauxite, which is mixed with lime (to control phosphorus impurities) and dissolved in a hot solution of caustic soda.⁵ This yields a soluble salt: sodium aluminate. Some of the alumina reacts with silica to form insoluble sodium-aluminum-silicate. This constitutes the greatest loss mechanism in the Bayer process, since the caustic soda could be completely recycled if it were not for the sodium combined with the silica. (In other words, the amount of caustic soda required is directly proportional to the silica content of the bauxite). A variant of the Bayer process for high silica domestic ore — the combination process — was developed in the U.S., but apparently it has not been significantly applied in western Europe. The undissolved residue, including iron and titanium oxides, is thickened, precipitated and filtered out, after which the solution is cooled to precipitate alumina hydrate. The latter is calcined to drive off the water and yield the dehydrated alumina that goes to the smelters.

Approximately 2.2 tonnes of bauxite (dry weight) are needed, on average, to produce one tonne of dehydrated alumina [Battelle 1975]. Three cases are described in *Table 2.3*, differentiated mainly in terms of the quality of the bauxite. With a high quality bauxite (1.922 tonnes per tonne of alumina) the other chemical inputs are limestone (39 kg) and caustic soda (39 kg) plus water. caustic soda (about 60 kg per tonne of alumina). A lower quality ore is also illustrated viz. 3.3 tonnes of bauxite per tonne of product. It requires 50.5 kg of lime (or 95 kg of limestone) and 113 kg of caustic soda per tonne of alumina output. However, another alternative is to start from soda ash (74.5 kg) and lime (38.5 kg). In this case, soda ash is reacted with lime to produce caustic soda on site [Battelle 1975 "Aluminum" Figure 3 p 150]. This case is illustrated in the flow chart *Figure 2.1* below. There are numerous possible combinations. In fact, every alumina plant is designed for a particular ore [Altenpohl 1982], which makes the industry relatively inflexible.

Table 2.3. Alumina via the Bayer process: 3 unit-process descriptions

A. Composite process derived from production data				
Utility inputs & outputs			Other uncouncted	
Electricity (input)	0.216	MWh	Water, process (input)	na
Heat (input)	15.630	GJ	Water, waste (output)	na
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Bauxite	1.922		Particulates, misc. aluminum	0.013
Limestone (CaCO ₃)	0.039		Red mud, sludge	0.969
Caustic soda (NaOH)	0.039		ALUMINA, ANHYDROUS (Al ₂ O ₃)	1.000
INPUTS ACCOUNTED FOR	2.001		OUTPUTS ACCOUNTED FOR	1.982
Source: authors		0.019	= Difference = .9% of Inputs	
B. Process as used in Europe as described in IDEA data base [Lübker et al 1991]				
Utility inputs & outputs			Other uncouncted	
Electricity (input)	0.364	MWh	Water, process (input)	na
Heat (input)	9.885	GJ		
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Bauxite	3.378		Particulates, misc. aluminum	0.530
Lime (CaO)	0.050		Red mud, sludge	2.027
Caustic soda (NaOH)	0.113		Water, waste	0.668
Starch	0.015		ALUMINA, ANHYDROUS (Al ₂ O ₃)	1.000
INPUTS ACCOUNTED FOR	3.557		OUTPUTS ACCOUNTED FOR	4.225
Source: [IDEA database]		0.668	= Difference = -18.8% of Inputs	
C. Balanced process (USA) described by Battelle				
Utility inputs & outputs				
Electricity (input)	na	na		
Heat (input)	na	na		
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Water, process	10.539		Red mud, sludge (inc 1.183 water)	1.9634
Bauxite (full wgt-dry=2.225)	2.557		Water, waste	9.516
Limestone	0.073		Stack loss (misc. Al particulates)	0.769
Sodium carbonate	0.075		ALUMINA, ANHYDROUS (Al ₂ O ₃ =99%)	1.000
Starch	0.006			
INPUTS ACCOUNTED FOR	13.249		OUTPUTS ACCOUNTED FOR	13.249
Source: [Battelle 1975, p.150]		0	= Difference = 0.0% of Inputs	

The Bayer process is quite energy intensive, due to the need to heat the caustic solution, and the various calcination stages. This energy — about 18.8 MMBTU per ton of contained aluminum in 1970 — is supplied by natural gas or other fuels. The alumina refining generates significant process wastes, especially in the mining and alumina production stages. A composite flow chart for primary aluminum production in the U.S. is shown in *Figure 2.2*.

The waste sludge from the Bayer process is called "red mud". The initial solids content of red mud before dewatering normally ranges from 17% to 20%. It contains insoluble oxides of

iron, silicon, titanium, and other trace metals as well as some aluminum silicate. Alumina may be recovered from the aluminum silicate by heating the red mud with soda ash and limestone, yielding a soluble sodium aluminum oxide and a calcium-silica waste called "brown mud". Titanium might also be recoverable from some red muds, but this is not economical at present. In fact, despite a great deal of research over six decades, no significant use has been found for this waste material. A possibility that has received some attention is to use aluminum ore as a source of the semiconductor gallium, which may find significantly greater uses in the future. This is discussed in a later section.

According to the U.S. Bureau of Mines anywhere from one third of a tonne to one tonne (dry weight) of waste red mud is generated per tonne of alumina produced. However, the second case described in *Table 2.3* generates much more waste, over 2 tonnes of red mud per tonne of alumina. The quantity of red mud obviously depends on the quality of the ore. The sludge is corrosive to the skin, due to residues of caustic soda used in the refining process. It is normally accumulated in settling ponds adjacent to the refineries. The caustic liquid can pollute surface or ground water. In dry climates, after some time for drying, the impounded area can be recultivated (though it is not very fertile). However in tropical regions of high rainfall, impoundment presents significant engineering problems and auxiliary treatment is likely to be needed to prevent ground-water contamination.

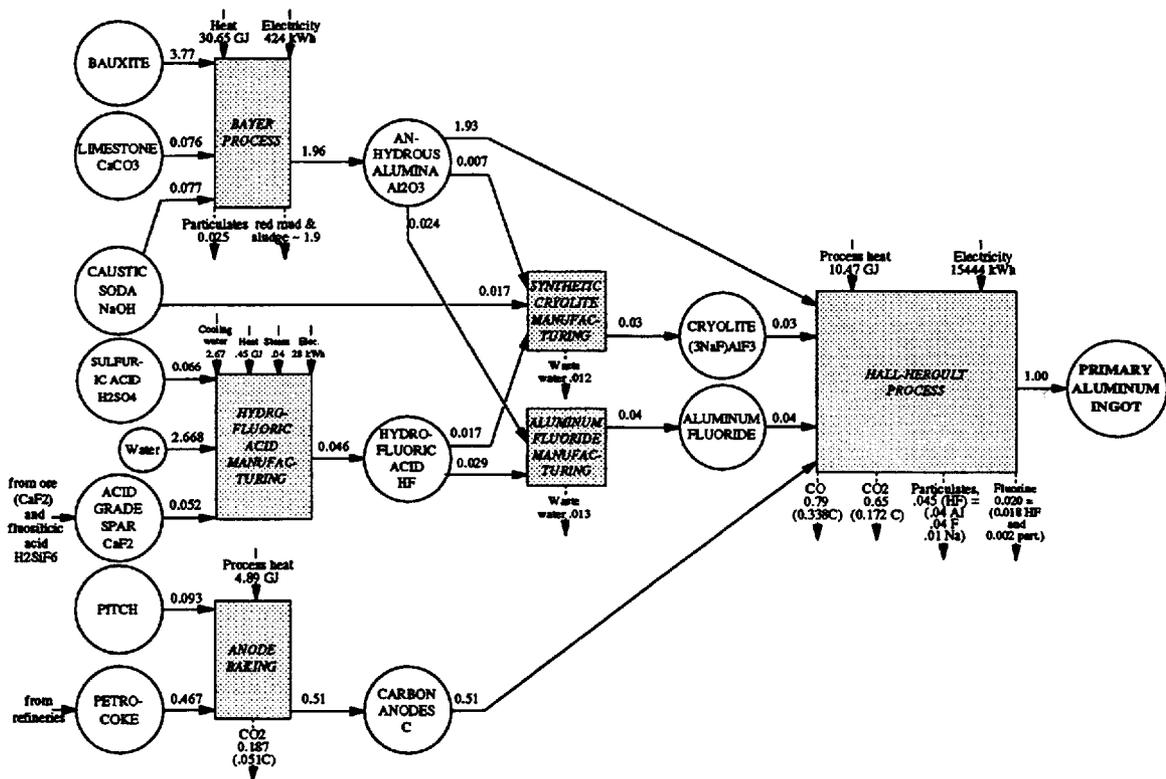


Figure 2.1. Composite aluminum ingot process. Data sources: various, 1970's

Alumina as such is used as an abrasive, as an adsorbent, and for chemical manufacturing, although an overwhelmingly large percentage of the output is currently smelted to produce aluminum metal.

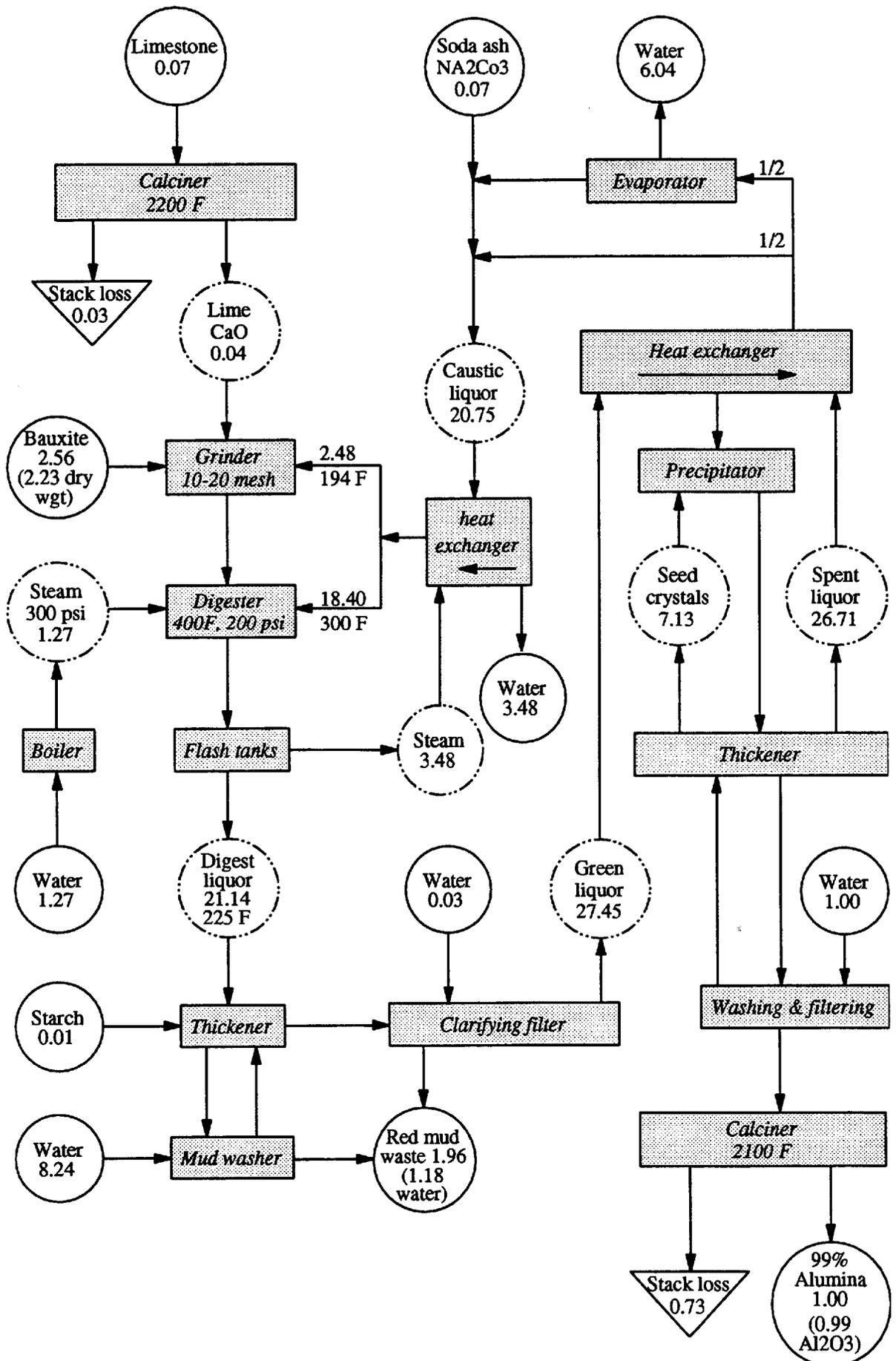


Figure 2.2. The Bayer process for producing alumina. Source: [Battelle 1975, p.150]

2.4. Aluminum Smelting Processes

The only process used for smelting aluminum today is the so-called Hall-Heroult electrolytic process. The alumina is dissolved in a bath of molten cryolite, which is sodium-aluminum fluoride (Na_3AlF_6), plus a small amount of aluminum fluoride, AlF_3 . Carbon anodes react with the alumina, generating carbon dioxide and metallic aluminum. Fluorine is also lost at the anode, partly as HF and partly as fluoride particulates. We have noted that the electrolytic reduction of alumina to aluminum requires significant quantities of electricity — of the order of 15,000 kwh per metric ton, at present. It also consumes petroleum coke (for carbon anode production). In terms of energy requirements, the last item amounts to 30 MMBTU per tonne of aluminum. The carbon combines with oxygen from the alumina in a fixed coke/aluminum ratio of 0.42. (We reconsider the carbon source problem later).

The Hall-Heroult smelting process also consumes aluminum fluoride, to make up for the fluorine lost from the electrolyte at the anodes. The estimated average (untreated) emission rate is 20 kg per metric ton of aluminum. (Actually, this is apparently an underestimate, for some smelters, as noted below). Industry practice in the U.S. in the early 1970's was said to recover about 70% of the fluoride emissions. In 1970 the U.S. Environmental Protection Agency (EPA) set the standard for control of new potlines at 95.5% or 1.8 kg/tonne of aluminum. Existing smelters were supposed to achieve about 90% control. The losses occur in two forms: gaseous HF and particulates. The gaseous emissions are considered most hazardous (especially to vegetation, and to animals that consume it) but it can be recovered most easily in wet scrubbers; dry scrubbers are much more efficient (up to 99%) for particulates. The two can be used in combination, but there is some tradeoff involved. Recovered fluorides can be recycled within the refinery, but this leads to a buildup of impurities in the aluminum. Elaborate methods of "ore management" are then needed to maintain aluminum product purity at the desired (99.9%) level.

European smelters capture and recycle some of their fluorine emissions, but not nearly up to the USEPA standard. The 1991 average makeup AlF_3 consumption for European smelters was 20 kg/tonne, with a range of 15 (Germany) to 26 (Italy) [ECOPLAN]. Estimated requirements for aluminum fluoride are given in *Table 2.4*. Aluminum fluoride consumes 6.5% of Western European HF and synthetic cryolite takes an additional 1.3%. Thus, nearly 8% of the fluorine consumed in Western Europe is used in the aluminum industry. (For further discussion of fluorine, see *Chapter 7, Phosphorus and Fluorine*). Since it is not embodied in the product, all of this makeup fluorine is either accumulated in a solid waste of some kind (e.g. water treatment sludge) or dissipated into the environment as air or water pollution.

An alternative to the Hall-Heroult electrolytic cell that promised to reduce electric energy consumption by 30% was (and is) the so-called ALCOA process. Instead of dissolving alumina in cryolite, the general idea is to convert aluminum oxide (alumina) to aluminum chloride by direct chlorination [Battelle 1975], [Altenpohl 1982]. Then the aluminum chloride can be dissolved in an electrolyte consisting of sodium and calcium or lithium chlorides. It can then be electrolytically reduced, but at a temperature lower than that needed for the Hall-Heroult process. More important, the bipolar chloride cells can be "stacked", unlike the Hall cells, thus reducing the voltage requirements and the resistance losses. The process releases chlorine at the carbon anode for recycling. ALCOA had a pilot plant in operation at Palestine,

Texas, from 1976 to 1981, but according to a company insider, the process was never been implemented in full scale operation due to a major strategic change of direction in the company (putting much more emphasis on downstream aluminum products and less on primary production). Nevertheless, it continues to attract interest.

Table 2.4. Western European production & consumption of AlF_3 , HF & Acid Spar 1991 (kMT)

Country	AlF_3 1991		HF 1991	Acid Spar 1991	
	Production	Consumption	Production	Production	Consumption
Austria		1.6			
Belgium			5.0		(a)
France	40.0	7.5	34.4	64	72.2
Germany (W)		11.0	72.9		153.1
Germany (E)					
Greece		3.0	8.8		18.5
Iceland					
Ireland					
Italy	10.0	6.0	54.4	16	114.2
Netherlands		5.7	7.2		15.1
Norway	16.3	16.0		16	
Spain	11.0	9.0	25.2	18	52.9
Sweden	17.7	1.9		(b)	
Switzerland		1.2			
United Kingdom		6.7	57.6		121
W. Europe	95.0	69.6	265.5	124+(b)	547

(a) from fluosilicic acid

(b) +16 kMT fluosilicic acid

One problem that arose with the early versions of the ALCOA process was that chlorine reacted with the carbon anodes — made from petroleum coke — and generated trace quantities of chlorinated aromatics, such as PCB's [Jarrett 1982]. These would constitute a potential toxic pollution problem. On the other hand, it was believed that the PCB problem could be contained by suitable waste treatment [Jarrett 1994]. Also, of course, fluorine emissions would be eliminated automatically. A detailed tradeoff analysis would have to be undertaken, of course, before making any major investment in the new technology.

An interesting possibility that deserves more attention is to use aluminum chloride rather than alumina as a feedstock for the ALCOA process. In principle, aluminum chloride can be obtained from a number of sources, from clay to coal fly ash, by hydrochlorination or direct chlorination. The economics of this combination appear to be potentially favorable. The major difficulty here is that for the ALCOA cell to work, the aluminum chloride must be anhydrous. Unfortunately, aluminum chloride (like calcium chloride) happens to be extremely hygroscopic i.e. "water-loving". To dehydrate it is a non-trivial (and energy intensive) technological task. Nevertheless, this possibility is considered further in another section (See Chapter 13, Fly Ash).

Recovery of primary aluminum by thermochemical means, not requiring electrolysis, has been considered. Three such processes were described in a 1975 report to the U.S. Bureau of Mines [Battelle 1975]. They are the ALCAN process, the Toth process and the "monochloride process" of Peacey and Grimshaw. The ALCAN process, as described by Battelle [ibid] involves an electric arc furnace to smelt bauxite directly (with coke) yielding an aluminum silicon alloy. This was chlorinated in a reactor, and subsequently decomposed in a high temperature decomposer. A pilot plant was built, but later shut down because of stress corrosion problems. These were apparently solved, but the plant was never reopened. Details of the process are not available.

The Toth process, as then described, used manganese to reduce aluminum chloride. The details are somewhat complex [Peacey & Davenport 1974]. Manganese metal is produced in a blast furnace; it reacts with liquid aluminum chloride (Al_2Cl_6) at moderate temperature and pressure, reducing the aluminum as powder. The aluminum powder is separated by a cyclone from the (liquid) manganese chloride. Unreacted aluminum chloride is evaporated and returned to the purifier. The latter is then oxidized at high temperature, releasing the chlorine which is returned to the aluminum chlorinator. The source of aluminum was to have been calcined clay. Both alumina and silica are chlorinated, but the silicon tetrachloride is recycled to the chlorinator to suppress chlorination of the silica. Chlorinated aluminum is separated from the other chlorination products (iron, sodium, potassium, calcium, etc) by multiple fractionation and condensation stages. Most of the process steps take place at high temperatures.

The major disadvantages of the Toth process appear to be (i) complexity (ii) the likelihood of corrosion problems at the high temperatures involved (iii) significant losses of chlorine through chlorinated silica, iron and other minor contaminants and (iv) relatively high coke requirements. Three kg of manganese are needed to reduce a kg of aluminum metal, and the reduction of each kg of manganese requires 1.5 kg of coke. Thus the coke requirement alone would be 4.5 kg per kg of Al. Also, blast furnace manganese is not pure. It contains significant quantities of the carbide Mn_7C_3 , which would not be as effective a reductant for aluminum chloride. The losses of chlorinated by-products would constitute a significant problem for environmental control.

The monochloride process mentioned above has been tested on a laboratory scale [Peacey & Davenport 1974]. The process is superficially much simpler than that of Toth, though it does not yield pure aluminum, but rather an aluminum silicon alloy (less than 1% Si). In brief, hot Al_2Cl_3 is passed through a bed of calcined bauxite and coke at high temperature. The carbon in the coke combines with the oxygen in the alumina. Everything else combines with chlorine. A variety of gases are formed (as in the Toth process), consisting of CO, AlCl, $SiCl_2$ and $FeCl_2$. The hot gases are then decomposed by a spray of molten lead. The aluminum chloride is reduced to aluminum, which ends up floating on the lead. Separation is presumably by fractional crystallization. In equilibrium, the aluminum retains a small lead and silicon residue. Further purification is not discussed in the report. Of course, the use of lead suggests a significant environmental risk.

Still another class of thermochemical reduction processes has been analyzed in some detail by ALCOA, under cost-sharing contract to the U.S. Department of Energy (1977-1982). This contract was initiated in response to reports of a Japanese plan to undertake national level

R&D leading to a pilot plant and a commercial plant. The results of the study suggested that the production of aluminum or aluminum-silicon alloys by means of an oxygen-blown blast furnace would be practical. The output of the blast furnace would be molten Al-Si-Fe. This would be separated into two phases (Al-Si and Fe-Si) in a fractional crystallizer. The Fe-Si fraction (ferro-silicon) is a valuable product with growing markets. The Al-Si fraction would then be electrolytically separated to Si and Al in a membrane cell [Bruno 1982].

The major advantages seen at the time for the process would be that instead of using coke derived from petroleum, the process would directly utilize much cheaper low-grade coal refuse or even shale. It would also eliminate fluoride emissions. The blast furnace process would also cut down on bauxite requirements by substituting domestic clay or fly ash for imported bauxite. Finally, the process would have been considerably less energy-intensive than the Hall-Heroult process, viz. 105-133 MMBTU/tonne of aluminum, vs. 192-232 MMBTU, depending on details.

2.5. Carbon vs. Inert Anodes

It was noted above that the Hall-Heroult process requires 0.42 tonnes of petroleum coke per tonne of primary aluminum smelted. There are two established processes for manufacturing carbon anodes. The older is the so-called Soderberg process, consisting of a single carbon anode that is fed continuously into the cell and is baked in-place by the heat of the cell. The Soderberg process has been replaced in virtually all modern plants (except a few in developing countries) by the pre-baked type of anode, which pollutes less and has higher electrical efficiency. Pre-baked anodes are made and baked outside the electrolytic cell.

Pre-baked anodes can only be made from petroleum coke made by a special process in which the hydrocarbon feed is preheated and "flashed" into a cold chamber, depositing carbon granules on every surface. This finely divided carbon is then ground, calcined and mixed with pitch and made into a paste, which is then baked.

Petroleum is not in short supply at present, but a future "oil crisis" cannot be ruled out. In any case, it would be useful either to find a cheaper source of carbon for anode production or to avoid the use of carbon anodes altogether. There are two attractive possibilities here. The first is to learn how to make carbon anodes with the desired electrical properties from a cheap source of carbon. The second is to learn how to make inert (non-reactive) permanent anodes that are not consumed in the electrolysis process.

The first approach may be nearer to realization. The starting point could be solvent-refined coal (SRC), which would permit removal of ash and sulfur prior to combustion, yielding solid briquettes of "coke" and a liquid hydrocarbon comparable to crude petroleum. This liquid can be refined like oil. It would seem to follow that petroleum coke could be produced from it by the same process that is now used in oil refineries.

The possibility of developing an inert anode for the Hall-Heroult cell has attracted the attention of researchers for a long time. Unfortunately, while there has been progress, the fundamental problem — corrosion — has not yet been solved. It is rumored that Vittorio de

Nora, the Italian inventor of the mercury cell for chlorine electrolysis, has been working on the problem in recent years. Confirmation is entirely lacking, however.

2.6. Concluding Remarks: Aluminum Production Technologies

Surprisingly, there are a number of promising new technologies for the alumina-aluminum industry. These range from new sources of alumina and petroleum coke to new smelting processes. In most cases some additional research or engineering development is needed, though in some cases — notably the ALCOA process — the remaining technical problems appear to be soluble. The major problem here may be to find the capital to scale up from the pilot scale to the industrial scale.

The fact that these new technologies have not been commercialized, in most cases, does not imply that the processes in question are faulty, though they are still largely untested and some will surely fall by the wayside. Industry spokesmen and neoclassical economists invariably claim that "if the technology was superior it would be in use today". Neoclassical economists tend to believe that capital markets, in particular, operate efficiently and therefore rational managers would make such investments if they were economically justifiable. This claim is naive and easily refuted. There are many examples in a variety of industries of admittedly superior technologies that have been, and still are neglected. This may occur for perfectly rational reasons, e.g. because they would require massive new investment and therefore cannot compete with a fully depreciated older plant (see, for example *Chapter 9. Chlorine*), or for much less rational reasons, such as personal experience (on the part of the managers) with the older technology.

In the aluminum case, of course, the new technologies have not reached the point of being widely accepted as superior. However, neither does their neglect to date prove inferiority. It can be laid to the fact that the relevant industries — notably electric power and primary aluminum — are generally mature, slow growing (or non-growing), oligopolistic, and extremely risk averse. The conditions (OPEC cartel, possible bauxite producers cartel) that stimulated a number of research projects in the 1970's did not last long enough to see any of the projects to completion. Nevertheless, future crises of a similar kind may occur.

2.7. Gallium Sources, Uses and Losses

Gallium is a transition metal whose properties make it potentially very valuable for high speed switching devices and lasers. It is not extraordinarily rare — 15 ppm in the earth's crust, as compared to 16 ppm for lead — but is rarely found in high natural concentrations. It is most conveniently extracted as a trace contaminant in aluminum ores (bauxite), although it is also potentially recoverable from zinc ores, phosphate rock and from coal fly ash.⁶ Typical gallium content of bauxites ranges from 30 ppm to 80 ppm. Among the large-scale bauxite producers, Surinam has 80 ppm, India 70 ppm, Australia, Jamaica and China 60 ppm, Brazil and Guyana 50 ppm, Guinea and Venezuela 30 ppm [USBuMines IC 9208].

There is one small copper-zinc-germanium-gallium-silver deposit in Nevada (Apex) where the gallium content of the ore, as originally graded, is 0.039% (3900 ppm) [USBuMines]. The mine has been closed since 1987, however. Even richer germanium-gallium ore — up to 1.85% gallium) has been found in small quantities at Tsumeb, Namibia.

A number of proprietary processes have been developed for extracting the gallium from Bayer process liquors, mostly by electrolysis or electro-deposition. Solvent extraction is also used. Virtually every producer has its own process variant. Major gallium producers or refiners in Europe in the 1980's were Rhone-Poulenc (using feedstock from Pechiney in France), AluSuisse (a refiner), VAW in Germany (which supplies feedstock to Ingal (International Gallium) GMBH in Germany, and Elkem in Norway [Roskill 1990]. In 1990 Elkem closed its operation and Rhone-Poulenc shifted its production from France to a new 50 tpy plant in Australia, using feedstock from ALCOA; in 1994 Rhone-Poulenc purchased the Ingal facility [Kramer 1994]. Sumitomo is apparently also a gallium producer.

Annual worldwide *potential* gallium production capacity, based on existing alumina capacity, exceeds 4000 tonnes/y (if all bauxite mines were operating at full capacity). On the other hand, *actual* world production capacity in 1993 was estimated to be 145 tonnes, including Rhone-Poulenc's Australian facility, plus 30 tpy capacity in the former USSR, 20 tpy capacity in Germany and 7 tpy capacity in Japan [Kramer 1994]. Actual world production in 1993 was only 35 tonnes [ibid]; U.S. consumption was just over 11 tonnes almost entirely for gallium-arsenide and indium-gallium-arsenide semi-conductor applications, such as lasers, light emitting diodes, photo-detectors and photovoltaic cells, and integrated circuits. By comparison, world consumption of electronic grade silicon in 1988 was roughly 750 tonnes; current consumption is somewhat larger (See *Chapter 11, Silicon*).

A few years ago it was thought that gallium-arsenide based semiconductor technology was on the point of replacing silicon-based semiconductor technology for integrated circuits, due to the fact that gallium arsenide circuit elements are undoubtedly faster. (They are also more radiation-resistant, which tends to make them the choice of preference in most military equipment). As regards integrated circuitry, the expected general substitution did not occur, however, because of continued improvements in silicon technologies. Other applications of gallium arsenide and indium-gallium-arsenide, for opto-electronic devices, continue to appear promising. A "day of gallium arsenide" may yet come. Nevertheless, advances in micro-miniaturization keep reducing the quantity of semiconductor material required per circuit element. Taking this into account, current sources of gallium (from bauxite, zinc ores and coal ash) appear to be ample for the foreseeable future. Thus, a potential need for gallium cannot justify large scale bauxite mining.

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Endnotes(2)

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2. Alunite is a potassium-aluminum sulfate. It is mined in the Zaglik district of Azerbaijan. Potash (for fertilizer) is a useful by-product of alumina operations.
3. Some alumina is, or has been, produced in Russia from nepheline syenite, mined in the Kola peninsula, and in Siberia. Nepheline concentrate contains 28-30% alumina. It is processed by sintering with lime, followed by leaching to remove the carbonates, followed by a second lime sinter to yield cement. For each tonne of alumina

produced, the nepheline process also yields 9-11 tonnes of Portland cement, 600-800 kg of sodium carbonate (soda ash) and 200-300 kg of potassium carbonate (potash).

4. An interesting possible process for producing sulfur, alumina and portland cement from fuel gas desulfurization (FGD) scrubber waste and kaolin, was proposed by TRW Inc. [Motley & Cosgrove 1978]. It is discussed in more detail in connection with #5 Sulfur. Another possible source of alumina is coal fly-ash. We discuss this possibility subsequently (#13). The major advantage of both of these schemes is that they would make bauxite mining essentially unnecessary while simultaneously converting waste materials (FGD scrubber waste and ash) into resources.
5. The production of alumina from bauxite currently consumes 6% of all the caustic soda produced in Europe. (See *Chapter 9, Chlorine*).
6. As a matter of interest, the average gallium content in U.S. coal ash is about 65 ppm. In some coal ashes gallium has been found in concentrations up to 1000 ppm (0.1 %) [Roskill 1990]. Recovery potential is based largely on the fact that gallium is further concentrated in flue dusts (fly ash). A recovery process for gallium and germanium was developed in the U.K. by GEC Research Laboratories and Johnson-Matthey & Co. It was operated commercially between 1950 and 1970 [ibid p. B8]. (See *Chapter 13, Fly Ash* for more detail).

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