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GLOBAL CONSIDERATIONS OF ALUMINIUM ELECTROLYSIS ON ENERGY AND THE ENVIRONMENT

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<u>Abstract</u>

Aluminium production requires resources in the form of energy and minerals, and the by-products of the process have an impact on the environment. Important tasks for the aluminium producers are to use the energy and the raw-materials more efficiently, and to reduce the amounts of various harmful gaseous and particulate emissions and their negative effects on the surroundings. The ways that the aluminium producers can contribute to lower the total energy consumption and reduce the emissions, are reviewed and discussed.

Introduction

One of the most important challenges for the aluminium industry in the future is to reduce the environmental damage associated with the production processes. The Hall-Héroult process still causes pollution problems, even if cell emissions have been reduced considerably in recent years. With the increasing global concern for the environment, it is necessary to focus on ways to improve the situation. The relationship between energy usage and impacts on the environment is recently receiving more attention. It is the purpose of the present contribution to describe the main problems on energy consumption and environmental performance, particularly for the smelting step of the aluminium production and for the electric power production. Possible means to remedy the situation will be reviewed and discussed.

1. ENERGY CONSUMPTION

Focus on energy saving

Since the significant rise in oil prices which began in the early 1970s, energy conservation has been a major concern of industrial

corporations, as well as many politicians, journalists and environmental protection organizations. The aluminium industry, as all other industries, has been called upon to save energy, but suggestions as to how this might be done have been few. The means of persuasion in many countries have been to increase taxes on most forms of energy. Taxes on energy is based on the underlying philosophy that the current energy prices do not reflect the hidden costs to the environment.

Energy taxation

One problem is that these taxes presently vary considerably between various countries. Steep taxes on energy may cause economic hardships and may therefore be rejected by many nations. As an example, Norway has recently restructured its tax policy on electricity. Elimination of the previous energy-consumption tax, which represented about 7 to 8% of the aluminium price, has now been replaced by a tax on the production of electricity. The total effect is a reduction in energy taxation by about 75% for Norwegian aluminium producers.

Recycling

A major energy saving can be made by recycling aluminium. Generally, recycling may also reduce the amounts of raw-materials used and the environmental pollution problems caused by primary metal production. Reusing aluminium by remelting and casting requires only 5-8% of the original energy input of aluminium produced from bauxite, see Fig. 1. Thus, with respect to energy saving and conservation, recycling of aluminium is highly beneficial, because about 95% of the energy is saved. Aluminium then may be considered as an "energy bank".

The electrolysis process

Fig. 2 shows the reduction in energy consumption of Hall-Héroult cells over the years, according to Haupin (1). Presently, energy

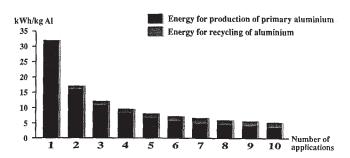


Figure 1: Average energy consumption per number of applications of recycled aluminium.

consumption for the electrolysis process varies in the range from 12.9 to 19.0 kWh/kg AI, depending on cell design and operation (2). From these data we calculate that 15.4 kWh/kg AI is the average value on a tonnage weighted basis, taking into account the larger tonnage produced by the most modern cells with the best available technology. An "industrial average energy consumption value" of 15.0 kWh/kg AI has been estimated previously (3). Shut-down of old and obsolete smelters and building of new cell lines with modern technology will continue, together with extensive retrofitting and modernization of existing smelters. This technology renewal process is slow, particularly due to the high investment costs of new capacity. However, it will give a small, but steady reduction in the "industrial average" energy consumption.

Energy conservation in the primary aluminium industry can be achieved through the following means, with predicted energy savings (4):

- Good housekeeping, 2-3% (improvements in monitoring and control).
- Retrofit, 10-15% (improvements in existing equipment efficiency).
- New technology, 15-30% (Best Available Technology, BAT).

If we again use the data collected by Pawlek (2), we may calculate that on a tonnage weighted basis, the best third of the world's smelters operate with an average energy consumption of 13.9 kWh/kg Al, the second third at 15.0 kWh/kg Al, and the last third at 17.2 kWh/kg Al. The three above-mentioned means, applied to these three groups of smelters, respectively, could then bring the "industrial average" energy consumption down towards 13.5 kWh/kg Al, or about 10% lower than the present average value. Jarrett (5) predicted an "industrial average value" of 14.3 kWh/kg Al in the year 2000. But beyond that, we cannot expect large

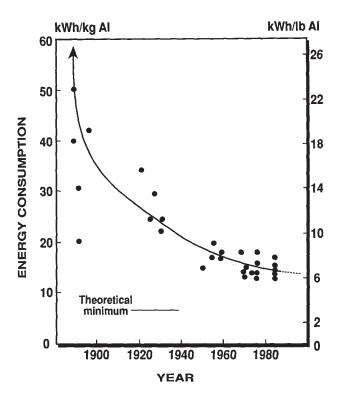


Figure 2: Energy consumption trend of Hall-Héroult cells, from Haupin (1).

energy savings from the Hall-Héroult process, unless a technological break-through is achieved, like the introduction of inert anodes and cathodes in bipolar cells. These improvements may still be some years ahead, however.

Carbon anodes

The main constituent of the carbon anodes is calcined petroleum coke. Coking is used to upgrade "waste" products from oil refineries, that would otherwise have to be sold as low-value fuels. The other important constituent of the anodes is coal tar pitch, which is distilled from the tar evolved when coke for the steel industry is made from bituminous coal. In the cells these anodes have a net consumption of 400 to 500 kg C per tonne of Al produced, which give a carbon mass consumption efficiency of 70% to 80%.

Energy efficiency in the ulilization of carbon anodes

The amount of electrical energy required in Hall-Héroult cells is reduced by use of consumable carbon anodes. The thermal energy content of carbon saves electrical energy. Let us therefore look at the energetic efficiency with which the carbon is burned. The reaction:

$$C(s) + O2(g) = CO2(g)$$
 (1)

has a standard Gibbs energy corresponding to 1.03 V, which is the $\underline{\rm emf}$ of a reversible fuel cell burning carbon to $\mathrm{CO_2}(g)$. This represents depolarization due to the carbon anode, as shown in Fig. 3. In the present Hall-Héroult cells half of it is lost in the overpotential on the carbon anode, but it still leaves 50% energy efficiency in the utilization of carbon. This is much better than can be achieved in a thermal, coal-fired power station. If we take into consideration that the overpotential generates heat which is necessary to balance the heat losses of the present process, the energy efficiency of the carbon anode will be about 80%.

In a future cell design with inert anodes, the decomposition voltage of alumina will increase by 1.03 V, as seen from Fig. 3. The anodic overpotential will then be 0.1 V, and with a stable titanium diboride cathode the interpolar distance may be reduced to about 15% of the present value (5). This may give a net reduction in cell voltage of about 0.3 V and a total energy consumption of 12 kWh/kg AI.

Electric power generation

The primary source of electric power and the power ownership are most influential on the price of the power and thereby on the economics of aluminium production. World-wide, the primary sources of electric power for aluminium production are as follows, when figures from Russian plants are included:

Source:	Percentage:		
Hydro	57%		
Coal	33%		
Nuclear	5%		
Gas	4%		
Oil	1%		

Over the past ten years, there has been sharp reduction in oil and natural gas consumption, which are compensated by pronounced increases in coal-fired and hydro-power generation. The share of nuclear power generation for the primary aluminium industry has remained stable.

Total energy consumption

Fig. 4 illustrates the <u>total</u> energy consumed in aluminium production based on alternate sources of electricity. The data include mining, ore preparation, reduction, casting and finishing. Clearly, the reduction step represents the largest variation. A thermal conversion efficiency of 33% is assumed for plants using non-renewable power sources. This is typical for a lot of installed

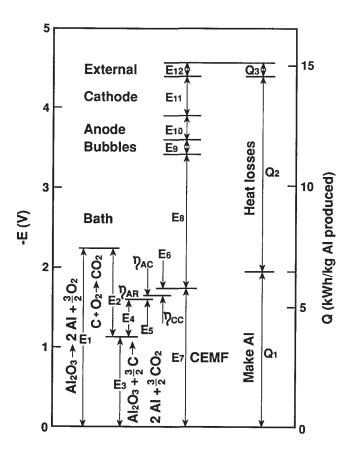


Figure 3: Typical voltage distribution and energy requirements in a Hall-Héroult cell.

plants, although modern thermal conversion efficiencies can be higher. The total energy requirement is reduced from 73 to 34 kWh/kg Al by changing from coal-based to hydro-based electric power. From an energy viewpoint it would therefore be advantageous to use hydro-electricity, and the world average of about 50 kWh/kg Al could then be reduced considerably. However, even if it is in this area that the greatest potential for energy savings exists, the conversion to hydro-power would involve large practical problems in many countries.

New smelter projects

Countries offering competitive rates for electric power, like Australia, Brazil, Canada and Venezuela, have the possibility to attract new aluminium smelters. The latter three countries have relatively cheap hydro-electric energy. Particularly, locations in regions of both abundant and low-cost power supplies will be advantageous, for example in South America and Africa, where a vast potential of unused hydro power is available. In 1987, Castells (6) claimed that Venezuela then had the world's lowest cost for hydro-electric power, with 6 mills per kWh, while the world-wide average cost at that time was 15 mills per kWh.

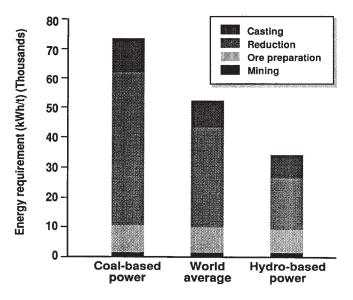


Figure 4: Total energy consumption of aluminium production for alternate sources of electric power (7).

In Venezuela it now seems that only one smelter project with a capacity of about 200 000 t/y, may be realized before the year 2000. Three smelter projects are currently under consideration in Chile, and a new smelter in Iran may come on stream in 2 to 3 years. These may be based on hydro power. In Africa a new smelter is under construction in Nigeria, where the power source will be natural gas, and a large expansion of Alusaf in South Africa (~ 470 000 t/y) is expected to be completed in 1996 or 1997, on the basis of thermal (coal-fired) power. Also the expansion of the Boyne smelter in Australia will be based on coal-fired power. Thus, about 1 million t/y of new aluminium smelter capacity is expected to come on stream before the end of the century, and less than half of this will be using hydro power.

Advantages of hydro power

Cost and availability of electric energy will continue to be of significant importance to the primary aluminium industry, and will override both market demands and national priorities. The advantages of hydro power; the use of a renewable source (water) at an energy efficiency of at least 90% and with no $\rm CO_2(g)$ or other pollutants emitted to the environment, make it unmatched as the most favourable energy source at present. The best policy in a global perspective would then be to build all new smelters in countries with sufficient supply of hydro power. This will probably never happen, mainly because many countries simply do not have the natural resources needed for building of hydro power stations. However, one solution may be to replace coal-fired power by hydro power imported from other countries.

As discussed above, only about half of the new aluminium capacity expected to come on stream in the near future, will be based on hydro power. If we look beyond the turn of the century, the percentage of aluminium production tonnage based on hydro power will probably remain between 50 and 60%. This reflects the availability of energy sources in the world. Undoubtedly, if this share could be increased, it would contribute to reduce the emissions and hence the adverse environmental effects of aluminium production.

2. EMISSIONS FROM ALUMINIUM SMELTERS

Introduction

In the past, the main concern for the environment was locally around the smelters, with focus on the fluoride emissions from the reduction cells. The smelters have now made significant achievements in reducing these emissions, and in several cases they have come further than the authorities have required. Certainly, the systematic work on emission-reducing measures will continue. Possibly the future threshold limit values for fluoride emissions may be based more on the tolerance of the natural local environment and the minimum levels of pollutants that do create damage, rather than on the technical capacity of the dry scrubbing systems.

Presently, global environmental concern has increased tremendously because of rising levels of $CO_2(g)$ and also $CF_4(g)$ emissions, which may contribute to global warming. The lower atmosphere and the surface of the earth are kept warm by what is popularly known as the "greenhouse effect". The reduced heat radiation away from the earth by clouds and gases in the atmosphere may then lead to an increase in the average surface temperature, like the glass of a greenhouse.

Global air pollution from smelters and from production of electricity

The three main climatic gases emitted from alumina reduction cells are:

- CO₂(g), typically 80-90% of the anode gas content during normal cell operation,
- CO(g), normally 10-20%, but up to 60-70% during anode effects,
- CF₄(g), evolved only during anode effects (15-20%).

CO₂(g)

This gas is the largest contributor to the "greenhouse effect", together with water vapour. $CO_2(g)$ is the main component of the anode gas during electrolysis, and clearly the amount of $CO_2(g)$ formed is directly proportional to the amount of aluminium produced. Thus, any further improvements in existing cell technology cannot be expected to reduce the $CO_2(g)$ formation from aluminium smelters, unless inert anodes and thereby $O_2(g)$ formation can be technically feasible. On the other hand, a considerable reduction may be achieved by conversion from coalfired to hydro-electric power generation, as will be discussed below.

For the further discussion, we will consider specifically the situation in Norway. The Norwegian Parliament has made a resolution with the aim of keeping Norway's total emissions of $CO_2(g)$ throughout the 1990s at the same level as in 1989, which means about 35 million tonnes per year. Norway is not a large contributor on a global basis, however. The $CO_2(g)$ emissions from Norway amount to only 0.2%, while for example USA emits about 25%. However, pro capita Norway has a relatively large emission, compared to many other countries.

Various means are considered in Norway to avoid any further increase in the $CO_2(g)$ emissions. The car traffic releases about one-fourth of the total Norwegian emissions of $CO_2(g)$, and an extra tax has now been added to the price of gasoline. Another "carbon tax" of about 0.1 USD per m^3 of $CO_2(g)$ emitted from the industry, has been suggested by Norwegian legislators, among various other means to reduce the $CO_2(g)$ emissions. However, it may not be very likely that Norway would introduce a one-sided "carbon tax". Such a tax system should in case involve all countries with production processes that emit $CO_2(g)$. That may then reduce the total emissions of $CO_2(g)$, which in turn may be favourable for the "greenhouse effect".

The twelve member countries of the European Community have also decided to stabilize their $\mathrm{CO_2}(g)$ emissions at the 1990 level until the year 2000. More controversial is the suggested introduction of a $\mathrm{CO_2}(g)$ tax of 3 USD per tonne of oil equivalents, which then will be increased successively to 10 USD at the end of the decade. Also other measures are being discussed at present, for example a combined $\mathrm{CO_2}(g)$ and energy tax.

Let us then look specifically at the present situation for the aluminium smelters. From the overall production reaction:

$$1/2 \text{ Al}_2\text{O}_3(s) + 3/4 \text{ C}(s) = \text{Al}(l) + 3/4 \text{ CO}_2(g)$$
 (2)

it is seen that 0.75 moles of CO₂(g) are produced for each mol of aluminium. With 100% current efficiency it is then easily calculated that 1.22 tonnes of CO2(g) are formed per tonne of aluminium produced. In practice, the best cells emit about 1.5 tonnes. If also the other CO2(g) emissions from the smelters are included (from anode production, cast house etc.), this value would be close to 2 tonnes per tonne of Al produced. Since the present annual world production of aluminium is about 19 million tonnes. the total CO₂(g) emissions from the aluminium smelters are 35 to 40 million tonnes per year. If the above-mentioned "tax" proposal should be introduced, it would constitute approximately 5% of the production costs for aluminium, and would therefore mean a significant economical burden. The future economics of aluminium production might then suffer. This new tax base might eventually make the Hall-Héroult process uneconomic under certain aluminium market conditions.

 ${\rm CO_2(g)}$ emissions are also strongly dependent on the source of electric power. Coal will release about 1 kg ${\rm CO_2(g)}$ per kWh of electrical energy produced, while natural gas releases about 40% of this amount. The corresponding emissions associated with hydro-electric power are negligible. This is shown in Table 1.

Fig. 5 illustrates how $CO_2(g)$ emissions depend on coal-based and hydro-based power generation. A dramatic reduction in the amount of $CO_2(g)$ per tonne of Al produced may be achieved by changing from coal to hydro-electricity. Modern cell technology with point feeding of alumina contributes to a further reduction towards 4 tonnes of $CO_2(g)$ equivalents per tonne of aluminium produced, when also the production processes for bauxite and alumina are included. This is only about one-tenth of the $CO_2(g)$ emissions from production of aluminium from coal-based power generation, as seen from Fig. 5.

It should be noted here that conversion from coal-fired to hydroelectrical power generation would contribute much more to reduce the total $CO_2(g)$ emissions, than would the introduction of inert anodes in the alumina reduction step. The ideal combination would be hydro-power and cells with inert anodes, which would give virtually no $CO_2(g)$ emissions. Relevant data are shown in Table 2

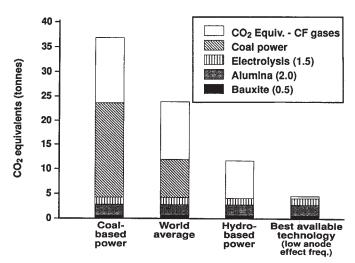


Figure 5: Total emissions of CO₂(g) from aluminium production for alternate sources of electric power (7).

Table 1. Data for CO₂(g) emissions from aluminium electrolysis, and from the corresponding electric energy production by various types of power plants.

CO ₂ emissions*	Hydro-electric or nuclear power plant	Gas-fired power plant	Coal-fired power plant
CO ₂ from electrolysis	1740	1740	1740
CO ₂ from electric power production	0	6160	15400
Total CO ₂ emissi (kg/tonne Al)	ons 1740	7900	17140
*Assumptions:	Anode consur (industrial ave Gas-fired po CO ₂ /kWh.	mption 15.4 kW nption 475 kg C rage consumpti wer plant er ower plant er	c/tonne Al (2), on values).

CO(g)

CO(g) formation during aluminium electrolysis is also significant. A value of 340 kg CO(g) per tonne of Al produced has been estimated (4). This value may seem somewhat high compared to the $CO_2(g)$ emissions, but it is probably reasonably correct from measured amounts of CO(g) in the anode gas and the stoichiometry of the CO(g)-forming reaction. It is noted that a particularly large formation of CO(g) occurs in the cells during anode effects. Probably most of the CO(g) evolved from Söderberg cells will be burned to $CO_2(g)$ in separate burners before leaving

Table 2. Calculated $CO_2(g)$ emissions from a future aluminium electrolysis process in cells with inert anodes, and from the corresponding electric energy production by various types of power plants.

CO ₂ emissions*	Hydro-electric or nuclear power plant	Gas-fired power plant	Coal-fired power plant
CO₂ from electrolysis	0	0	0
CO ₂ from electric power production	0	4800	12000
Total CO ₂ emissions (kg/tonne Al)	0	4800	12000

* <u>Assumptions:</u> Energy consumption 12 kWh/kg Al. Anode gas formation 890 kg O₂ /tonne Al.

the stacks, and the CO(g) emissions will then be small. Also CO(g) from prebaked anode cells is probably oxidized rapidly, and the actual CO(g) emissions may perhaps be about 1% of the $CO_2(g)$ emissions. CO(g) is poisonous to humans, but it is diluted strongly in the working atmosphere. Furthermore, it does not contribute significantly to the "greenhouse effect".

CF₄(g)

 $CF_4(g)$ has for a long time been known to be formed during anode effects in Hall-Héroult cells, but only recently it has been found to be a very potent greenhouse gas, with an extremely long atmospheric residence time. The main problem here is the very high so-called "global warming potential" for $CF_4(g)$, which may be about 5 100 times higher than for $CO_2(g)$, according to recent data (8).

Gaseous carbon tetrafluoride is formed in the cells only during anode effects, and this is an important reason for trying to reduce the frequency and the duration of anode effects in the smelting process. With the best modern prebaked cell technology, the typical number of anode effects may be close to 0.1 per day, while the average value for all prebaked cells may be about 1. Older Söderberg and prebaked cells may have 2 to 3 anode effects per day. Thus, there will be considerable variation in $CF_4(g)$ emissions from plant to plant as the anode effect frequency varies between smelters. The duration of each anode effect is also very important,



because it is actually the time during which the cell is on anode effect, that mainly determines the amount of $CF_4(g)$ emission. For example, cells that have three anode effects per day, but are extinguished within 1 minute, may not be as bad as cells with one anode effect per day, but taking 4 minutes. Typical $CF_4(g)$ emission values have previously been estimated to 1.5 to 2.5 kg per tonne of Al produced (9), but data now being collected indicate that much less $CF_4(g)$ is evolved. Recent measurements from Hydro Aluminium's smelters show average emission values of 0.06 and 0.8 kg of $CF_4(g)$ per tonne of Al produced, for prebaked anode cells and Söderberg cells, respectively (8).

Gaseous dicarbon hexafluoride, $C_2F_6(g)$, is also formed only during anode effects, but in smaller amounts, only about 5 to 15% of the amount of $CF_4(g)$. The "global warming potential" for $C_2F_6(g)$ is about 10 000, but the quantities formed make a relatively small contribution to the "greenhouse effect", compared to $CF_4(g)$.

Regional air pollution from smelters

SO₂(g)

 $SO_2(g)$ emissions may give acid rain and cause damage to the vegetation. The major sources of sulphur in aluminium electrolysis are organic sulphur compounds in the petroleum coke and coal tar pitch used in the anode materials. These compounds react with alumina in the bath to form $SO_2(g)$. Hydro Aluminium's smelters use sea water or a basic aqueous solution in wet scrubbers to treat the $SO_2(g)$ -containing anode gases.

Local air pollution from smelters

The main emissions that cause air pollution in the immediate surroundings of an aluminium smelter are:

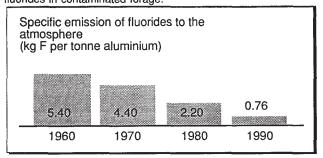
- Gaseous [HF(g)] and particulate [NaAlF₄(g)] fluorides,
- PAH compounds,
- Dust.

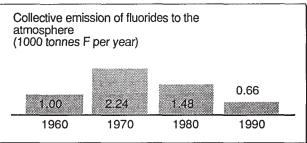
These will be discussed below, together with possible ways of reducing the amounts of these emissions.

Fluorides

These consist of gaseous fluorides, mainly HF(g) from reactions of the bath components with water or humidity (hydrolysis), and particulate fluorides formed by condensation of gaseous NaAlF₄(g), which evaporates from the bath (10). Restructuring, new and improved gas cleaning equipment, and continuous improvements in the smelter operation have contributed to reduce considerably the fluoride emissions from the aluminium smelters in Norway in the last thirty years, as shown in Fig. 6.

These emissions have been reduced from about 5 kg F/tonne Al in 1960 to 0.8 kg F/tonne Al in 1990. The present level is about 0.4 kg F/tonne Al for prebaked anode cells and about 1.0 kg F/tonne Al for Söderberg cells in Hydro Aluminium. Previous problems were mainly damage to vegetation and livestock in the neighbourhood of aluminium plants. Fluorosis in teeth and bones has been observed on farm and wild animals from ingestion of fluorides in contaminated forage.





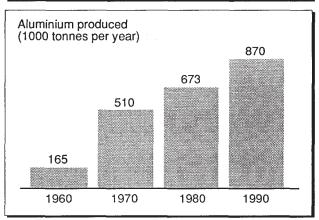


Figure 6: Fluoride emissions to the atmosphere from the Norwegian aluminium smelters since 1960.



PAH

Polycyclic aromatic hydrocarbons (PAH) emitted from carbon materials, mainly Söderberg anodes, have been strongly focused during the last decade. The PAH problem is mainly related to the use of coal tar pitch as a binder phase in these carbon materials. Among the fifty PAH components present in coal tar pitch, it has been verified that some of them have shown carcinogenic effects in animal tests. Health studies have not shown any increased risk of cancer for the workers and the local population around the Norwegian aluminium smelters. Hydro Aluminium has worked systematically on this problem for more than ten years (11).

Dust

In this connection dust is mainly fine-grained alumina. It arises from filling and discharge of alumina silos, and during transportation of alumina to the cell and feeding it to the bath. Dust also forms in the dry scrubber, and from ship unloading of alumina powder. Better housekeeping may reduce the adverse effects of airborne dust on the working atmosphere. This is really more of a welfare problem than a health risk.

Concluding remarks

Technological approaches to reduce the energy consumption and minimize $CO_2(g)$ emissions in connection with the aluminium electrolysis process may then be summarized as follows:

- use of surplus hydro-electric power potential,
- improved cell design and process control (Best Available Technology),
- better energy efficiency of the Hall-Héroult cells,
- new technology (inert electrodes).

It may be mentioned here that there are several technological solutions to reduce $CO_2(g)$ emissions and to remove $CO_2(g)$ from the atmosphere, but common to all of them is that they are very expensive with the use of existing technologies (12). Reduced $CO_2(g)$ emissions by increasing energy conservation could provide cost savings, although not necessarily lower product costs. The encouraging aspect of energy conservation is that it is both economically and ecologically sensible.

References

- W. Haupin, in <u>Hall-Héroult Centennial</u>, <u>First Century of Aluminum Process Technology 1886-1986</u>, ed. by W.S. Peterson and R.E. Miller, (Warrendale, Pa.: TMS, 1986), 106-113.
- R. Pawlek, <u>Primary Aluminium Smelters and Producers of the World</u>, (Düsseldorf, Germany: Aluminium-Verlag, 1986).
- 3. H. Kvande, Magyar Aluminium, 26 (1989), 382-389.
- 4. <u>Guidelines for Environmental Management of Aluminium Smelters.</u> United Nations Environmental Programme, Paris, 1986.
- N. Jarrett, in A.R. Burkin: <u>Production of Aluminium and Alumina</u>, (Chichester etc.: John Wiley & Sons, 1987), Chapter 13, 188-207.
- E.M. Castells, in <u>Documentation Volume from the 8th International Light Metals Congress</u>, Leoben-Vienna, (Ranshofen, Austria: Austria Metall, 1987), 177-181.
- K.S. Yoshiki Gravelsins, J.M. Toguri and R.T.C. Choo, "Metals Production, Energy, and the Environment, Part I: Energy Consumption", <u>JOM</u>, 45 (5) (1993), 15-20.
- I. Berge, R. Huglen, M. Bugge, J. Lindström and T.I. Röe, Light Metals 1994, paper in print.
- W.E. Haupin, in A.R. Burkin: <u>Production of Aluminium and Alumina</u>, (Chichester etc.: John Wiley & Sons, 1987), Chapter 12, 176-187.
- K. Grjotheim, H. Kvande, K. Motzfeldt and B.J. Welch, <u>Can. Met. Quart.</u>, 11 (1972), 585-599.
- 11. M. Skogland, Light Metals 1991, 497-502.
- 12. D. Forrest and J. Szekely, <u>JOM</u>, 43 (12) (1991), 23 -30.