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LIFE–CYCLE COMPARISON OF THE HALL–HEROULT PROCESS, INERT ELECTRODES, AND ENERGY SUPPLY IN ALUMINUM PRODUCTION

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Abstract: Aluminum (Al) production consumes 14 kWh of electricity per kg Al and produces 1.1 billion tonnes of carbon emissions ($CO_{2,eq}$) annually. The Hall–Heroult process is currently the only industrial process for Al production, producing two tonnes of $CO_{2,eq}$ per tonne Al by carbon anode electrolysis. Electrodes that do not participate in the electrolysis of alumina can reduce the impact of Al production. Transitioning to inert anodes implies redesign of electrolysis cells to optimize energy requirements. We performed a life–cycle analysis to compare the ecological footprint of Hall–Heroult and inert production using GaBi software and the ecoinvent database, complemented with primary data. Results were calculated for two Hall–Heroult and fifteen inert scenarios, varying power between 13.5 kWh and 17 kWh for six different energy mixes: Icelandic hydropower, global mix, natural gas, coal, nuclear, and geothermal. A final "best–case" scenario uses hydropower data as the power source for alumina refinement (shown in electrolysis) .The results reveal that the energy mix dominates the impact on the ecological footprint in the earlier refinement and electrolysis stages. However, using inert electrodes in smelters powered with renewable electricity can lower the carbon footprint of aluminum production by over 80%.
Keywords: aluminum production, inert anodes, LCA

INTRODUCTION

Aluminum production alone currently accounts for around 2% of global carbon dioxide emissions. To produce aluminum, bauxite ore is mined and refined to alumina, then processed by electrolysis requiring between 12 and 17 kWh per kg Al [8]. Conventionally, electrolysis requires anodes made of carbon, a feedstock of alumina (aluminum oxide), and electrical energy applied as a DC current in the Hall–Heroult process. The electrolysis produces pure liquid aluminum and carbon dioxide. Carbon monoxide is coevolved, as are smaller amounts of fluorocarbons and sulfur compounds due to impurities in the anodes.

$$1/2Al_2O_{3(solution)}+3/4C_{(s)}=Al_{(l)}+3/4CO_{2(g)}$$

and

$$1/2Al_2O_{3(solution)}+3/2C_{(s)}=Al_{(l)}+3/2CO_{(g)}$$

Carbon emissions also occur during the manufacturing of the carbon anodes [6].

Inert metal anodes (IMA), in place of carbon, can eliminate the carbon emissions from alumina electrolysis and limit those produced in anode production, substantially reducing the carbon footprint of the entire smelting process [8]. IMA evolve oxygen rather than carbon dioxide and other hydrocarbons.

$$1/2Al_2O_{3(solution)}=Al_{(l)}+3/4O_{2(g)}$$

Attempts to develop industry–level inert anodes with similar performance to the Hall–Heroult process started in the early 20th century. Anode research mainly focused on three classes of materials: ceramic, metal, and cermet [7]. In the 1990s The Aluminum Company of America – later, Alcoa – patented the process and apparatus for low temperature aluminum electrolysis, recommending the use of inert anodes composed of 17%wt Cu and 83%wt other oxides, namely NiO and Fe_2O_3. More recently, Padamata et al. confirmed the efficiency of Cu–Ni–Fe anodes in a 2018 review of industry progress. Cu–Ni–Fe anodes form protective oxide layers during electrolysis, slowing down the corrosive effects of the electrolyte [7]. Gunnarsson et al. (2019) revealed the production of Al with 99.22% purity using 20%wt Cu, 42%wt Ni, 38%wt Fe anode and TiB_2 cathode with a 21mm distance between vertical electrodes. This experiment produces low current efficiencies of 71–73%, but low rates of aluminum contamination by electrode material [2].

Directly substituting IMA into existing electrolytic cells would however increase the energy requirement for smelting plants by up to 25% as the reaction products are higher energy molecules [8]. Producing oxygen at the anode instead of carbon dioxide drives up the operating voltage by about one volt, corresponding to over a 3 kWh/kg Al electrical power increase [9]. According to Haupin and Kvande (2000), it is thermodynamically possible to operate inert anode cells at 13.2 kWh/kg Al by reducing the anode–cathode distance and thereby reducing the voltage drop across the electrolyte. Maintaining the power requirement at 13.5 kWh would require the electrolytic cells to be retrofitted [8]. In 1994, Moltech published U.S. Pat. No. 5,362,366 detailing an anode–cathode arrangement for non–consumable anodes and cathodes that maintains the efficiency of conventional electrolysis. These arrangements primarily allow the new electrodes to be positioned vertically in existing cells, with groups of inert anodes filling the place conventionally filled by a single carbon anode [10].

La Camera et al. (1995) also rely on vertical arrangements to obtain low–temperature electrolysis results in their 1995 patent. Brown (2001) shows that considerable energy savings of up to 30% can be obtained by using vertical electrode cells (VEC) over conventional arrangements while also limiting operating costs due to the reduced rate of anode replacement. However, he also outlines substantial engineering challenges related to the implementation of VEC, namely electrode manufacturing and alumina–feeder technology [1].

In total, alumina electrolysis requires an anode, cathode, electrolyte, container, method of delivering electricity, alumina feeder, and product extraction system. Out of these elements, it is reasonable to assume that the container, method of delivering electricity, alumina feeder, and product extraction system could remain constant in a retrofit. In addition to the environmental aims of IMA, they also represent a potential for financial and occupational improvement [5]. As IMA theoretically do not participate in the electrolysis reaction, their slow rate of decomposition eliminates many costs associated with frequent replacement of carbon anodes. Anode changing also creates the highest exposure of aluminum workers to particulate matter and toxic gases from the process, so IMA have the potential to improve working conditions in smelters as well [5].

Around 70% of the global carbon dioxide emissions from aluminum smelting currently come from the high electrical energy requirements of the process. The Life Cycle Inventory (LCI) data published by the International Aluminium Institute (IAI) reveals that the geographic location of aluminum smelters and the corresponding energy mix had a significant environmental effect [12]. In a comparative LCA of smelting technologies including pre–baked and inert anodes, Kovács and Kiss (2015) also emphasize the importance of energy mix. However, their LCA does not include emission values related to the retrofit of the smelters required to minimize energy consumption. There is a need to understand how the IMA electrolysis process partnered with the costs of a retrofit compare to the Hall–Heroult process with various energy inputs.

This study aims to focus on the advantages of IMA compared to the Hall–Heroult process and to calculate a full LCA for different energy sources and requirements. In this study, we calculated the LCA for fifteen scenarios, addressing an energy requirement of 13.5 kWh/kg Al, 17 kWh/kg Al (corresponding to roughly a 25% increase), and six different energy mixes.

METHODS

To compare the LCA of inert anodes, carbon anodes, and different energy mixes we developed fifteen realistic scenarios (Table 1). For comparative purposes, a GaBi flow was constructed for the Hall–Heroult process to ensure consistent inputs with the modeled IMA process, such as electricity inputs and material flow datasets. The results from this flow are included as Scenarios I and II.

Table 1. Hall–Heroult and IMA scenarios

Scen no.	Process	Power Requirement*	Energy Source
I	HH	14.1**	Hydro
II	HH	14.1**	Global
III	Inert	13.5	Hydro
IV	Inert	17	Hydro
V	Inert	13.5	Global
VI	Inert	17	Global
VII	Inert	13.5	Natural Gas
VIII	Inert	17	Natural Gas
IX	Inert	13.5	Coal
X	Inert	17	Coal
XI	Inert	13.5	Nuclear
XII	Inert	17	Nuclear
XIII	Inert	13.5	Geothermal
XIV	Inert	17	Geothermal
XV	Inert	13.5	Hydro***

* kWh per kg Al; ** European average; *** including adjusting the electricity input for the alumina refinement stage

The full LCA was established by the ISO 14044 standards to define a goal and scope of the study. GaBi software by Sphera (Sphera Solutions Inc., 2021) was used to model the LCA process chain, calculate the impact categories, and perform a sensitivity analysis.

Goal

The goal of this LCA was to fully characterize the effect of a transition to inert electrodes on the aluminum production process. Values obtained from the modeling of inert electrodes were compared to those in the literature relating to carbon anodes in the Hall–Heroult process.

Scope Definition

Five main unit processes were considered in the model: the electrolytic smelter retrofit process, inert anode manufacturing, inert cathode manufacturing, electrolysis, and inert electrode recycling. These processes occur within the aluminum production chain between the refinement of alumina and the casting of ingots.

This LCA represents a gate–to–gate model within the aluminum production process, although it contains a cradle–to–grave model of the inert electrodes themselves.

The functional unit for this LCA was defined as 1 tonne Al. This is consistent with other aluminum–related LCAs, such as the one performed by the International Aluminium Industry (*Life Cycle Inventory (LCI) Data and Environmental Metrics*, 2017). In the individual unit processes 1 kilogram Al was used, which was then scaled up in the larger LCA. Electricity inputs to the system were implemented at the highest level of the LCA for ease of comparison. Adjustments to the electricity inputs were critical in comparing Icelandic energy mixes to global energy mixes in the different scenarios considered for the results of this LCA.

Impact Categories

GaBi Software and ecoinvent environmental quantities were used to assess the environmental impact of the constructed flow. Of the significant number of options available in the software, six impact categories were evaluated:

i) global warming potential over 100 years (GWP100),
ii) primary energy demand (PED),
iii) human toxicity potential (HTP),
iv) acidification potential (AP),
v) terrestric ecotoxicity potential (TETP), and
vi) freshwater use.

Sensitivity Analysis

Three main parameters were chosen as the subjects of a sensitivity analysis: the energy source, the method of alumina refinement, and the amount of anode and cathode required per kg of Al. The GWP100 was chosen as the main indicator of environmental impact.

RESULTS

The results of the LCA from the fifteen scenarios described by Table 1 were evaluated regarding the six impact categories: GWP100, PED, HTP, AP, TETP, and freshwater use.

Global Warming Potential

The GWP100 was calculated and is displayed in Figure 1. The scenario with the highest GWP100 is Scenario X (inert, 17kWh, coal) at 21,881 kg $CO_{2,\ eq}$ per tonne Al while the scenario with the lowest is Scenario XV (inert, 13.5kWh, hydro) at 820 kg $CO_{2,\ eq}$ per tonne Al.

Primary Energy Demand

The PED was calculated for all scenarios. These results are shown in Figure 2. Scenario X (inert, 17, coal) has the highest PED at 319,584 MJ per tonne Al and Scenario III has the lowest PED at 80,052 MJ per tonne Al.

Human Toxicity Potential

In Figure 3, the HTP for the Hall–Heroult and IMA scenarios is displayed. The highest HTP is 17,505 kg DCB_{eq} per tonne Al for Scenario II (HH, 14.1kWh, global) and the lowest HTP is 2,992 kg DCB_{eq} per tonne Al for Scenario XV (inert, 13.5kWh, hydro).

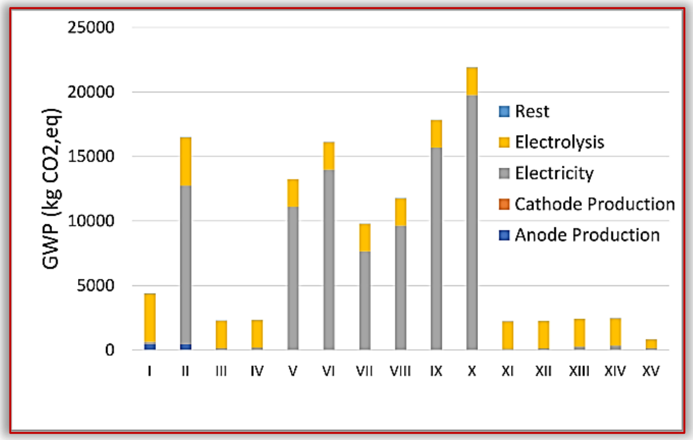

Figure 1. GWP100 for the fifteen scenarios

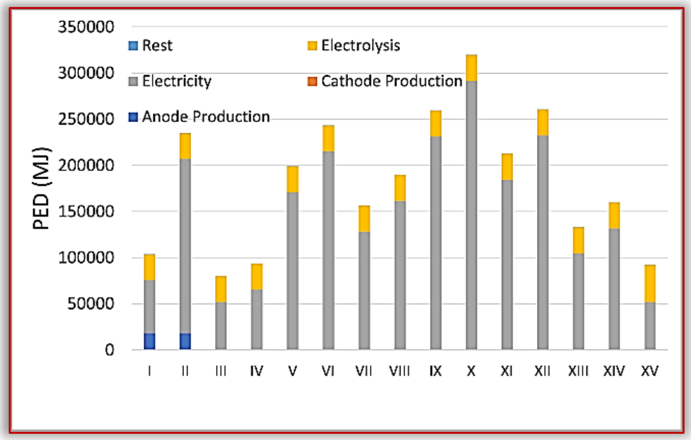

Figure 2. PED for the fifteen scenarios

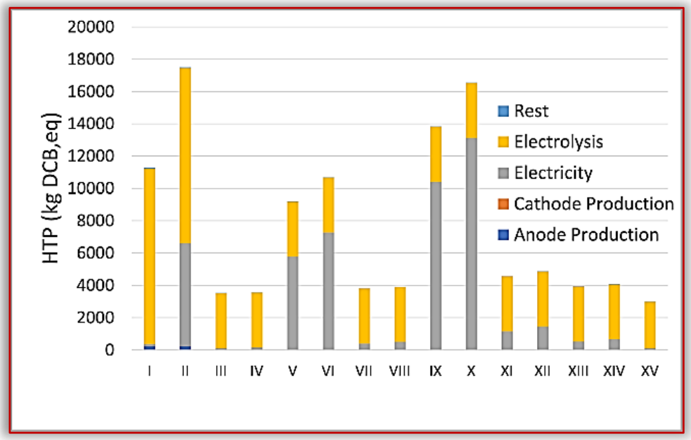

Figure 3. HTP for the fifteen scenarios

Acidification Potential

In Figure 4, the AP for the Hall–Heroult and IMA scenarios is displayed. The scenario with the highest AP is Scenario X (inert, 17kWh, coal) at 150 kg $SO_{2,\ eq}$ per tonne Al while the scenario with the lowest is Scenario XV (inert, 13.5kWh, hydro) at 15 kg $SO_{2,\ eq}$ per tonne Al.

Terrestric Toxicity Potential

In Figure 5, the TETP for the Hall–Heroult and IMA scenarios is displayed. Scenario X (inert, 17, coal) has the highest TETP at 70 kg DCB_{eq} per tonne Al and Scenario XV has the lowest TETP at 27 kg DCB_{eq} per tonne Al.

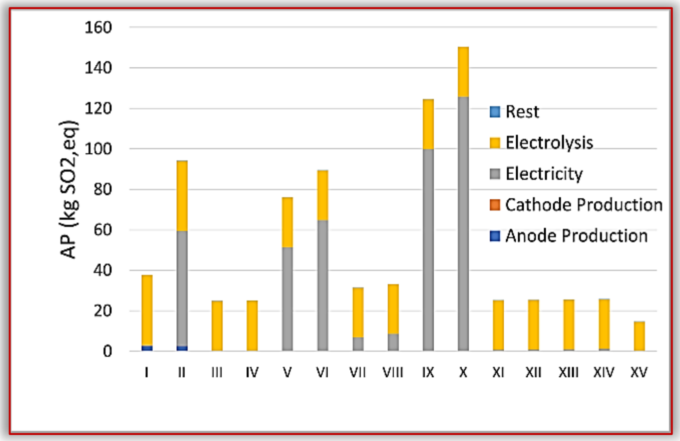

Figure 4. AP for the fifteen scenarios

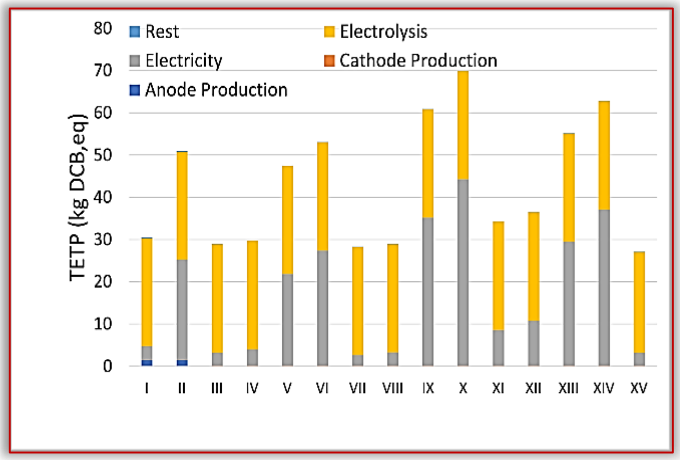

Figure 5. TETP for the fifteen scenarios

Freshwater Use

In Figure 6, the freshwater use for the Hall–Heroult process and the IMA scenarios is displayed. The highest freshwater use is 141,460,827 kg H_2O per tonne Al for Scenario IV (inert, 17 kWh, hydro) and the lowest freshwater use is 4,769,210 kg H_2O per tonne Al for Scenario VII (inert, 13.5kWh, gas).

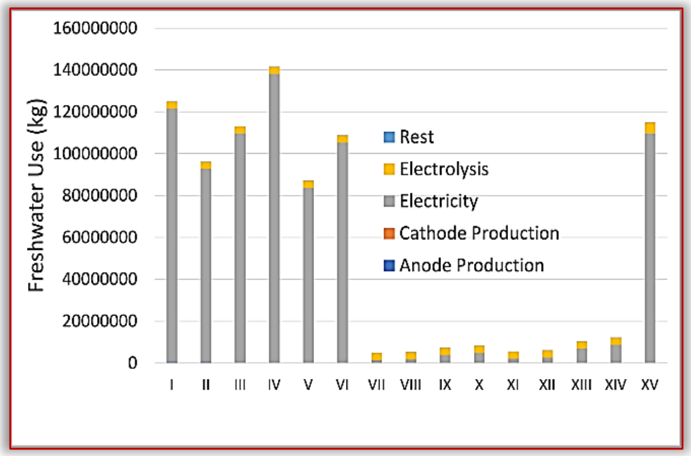

Figure 6. Freshwater use for the fifteen scenarios

DISCUSSIONS

Global Warming Potential

As expected, the transition to inert anodes offers significant $CO_{2,\,eq}$ emissions savings when the appropriate energy mix is used. Powering electrolysis with hydropower, much of the GWP in the HH process comes from anode production, direct emissions from the electrolysis process, and upstream emissions related to alumina production. Although the IMA process maintains these alumina–related emissions, the carbon emissions in the anode production and direct emissions from electrolysis are essentially eliminated. As relates to anode production, although the IMA technology this study is based upon require iron, nickel, and copper (metals not used in comparable quantities in the Hall–Heroult process) and so include in their LCA the corresponding production processes, this effect overall is quite small due to the anodes' long lifetimes and recyclability. The increase in energy requirement modeled in Scenario IV does little to alter these results when the energy source is Icelandic hydropower.

Using global energy mixes – Scenarios V and VI – alters these conclusions significantly. In Scenario V, GWP is still saved with a switch to IMA when the power requirement is 13.5 kWh per kilogram Al. As in Scenarios III and IV, this is primarily due to the reduction of emissions from the anode production and electrolysis processes. However, with the 17 kWh power requirement of Scenario VI, the GWP of HH and inert production become almost equal, with the HH process at 16,500 kg $CO_{2,\,eq}$ per tonne Al and the IMA process at 16,100 kg $CO_{2,\,eq}$. Scenarios VII to XIV display predictable results with coal–powered electricity producing the highest GWP, followed by natural gas, geothermal, and nuclear. Scenario XV displays the "best case scenario" for aluminum production, specifically for the case of alumina refinement in South America and smelting in Europe. These results were achieved by embedding hydropower data into the alumina refinement process, as well as maintaining the conditions from Scenario III. With a GWP of 820 kg $CO_{2,\,eq}$, Scenario XV represents an 81.4% GWP savings from Scenario I and a 64.0% GWP savings from Scenario III.

Primary Energy Demand

Following a similar trend to GWP, most of the PED savings offered by IMA come from the anode production stage. The fossil–based composition of carbon anodes adds significant chemical energy to the HH LCA and is eliminated in the IMA LCA, resulting in a 23.0% PED savings between Scenarios I and III. This percentage rises to 31.3% when the electrolysis portion of production is isolated by neglecting alumina refinement. For other scenarios, a general trend of PED due to energy source can be seen with coal as the highest, followed by nuclear, then global mix, then geothermal. Hydropower offers the lowest PED per tonne Al.

Human Toxicity Potential

The carbon anodes in the HH process are the primary cause of the sulphur and perfluorocarbon compounds that affect HTP. Due to this, Scenario III shows a 68.7% reduction in HTP over Scenario I. In this impact category, the electrolysis process appears as the most significant factor as Scenario II tops even Scenario X. However, fluoride present in the electrolyte is the source of hydrofluoric acid emissions and electrolyte composition and interaction for IMA electrolysis is still a point of continued research.

Thus, reliable estimates of the HTP reduction requires further study. For IMA Scenarios VII to XIV, energy source again determines the trend with coal followed by nuclear, then natural gas, then geothermal.

Acidification Potential

Again due to sulphur compounds present in carbon anodes, IMA are able to offer AP savings over the HH process, with Scenario III having 34.2% less AP than Scenario I. Even with a global mix energy source – Scenarios II and V – IMA offers a 19.3% reduction. Other energy sources cause a decreasing trend with respect to coal, natural gas, geothermal, and nuclear.

Terrestric Toxicity Potential

As with other impact categories, the lack of carbon anodes in the IMA process leads to a reduction potential in TETP. Between the hydropower scenarios I and III there is a 5.3% TETP reduction and a 7.0% TETP reduction between the global mix scenarios II and V.

Other scenarios are listed in terms of decreasing TETP according to their energy mix: coal, geothermal, nuclear, natural gas.

Freshwater Use

Common trends for other impact categories are slightly altered for freshwater use, as hydropower uses substantial amounts of freshwater to generate electricity. For this reason, scenarios that include hydropower production – I, II, III, IV, V, VI, and VX – are significantly higher than all other energy mix scenarios.

Sensitivity Analysis

When focusing on GWP100 as the main environmental indicator, it was found that the source of electricity had the most significant impact on the results. When the global mix energy input was varied by 50% against a default energy source of hydropower, it produced an 18.3% effect on the results. Although the variance of alumina input also had an impact – 5.18% variance of the results with a 50% variation – this can be viewed as a sub–case of power source variation, already identified as the most significant contributor to GWP.

Finally, the electrode input amount had an extremely insignificant effect on the results. This is not surprising, as the longer lifetime and recyclability of the anodes allow their effect to be minimized in the LCA.

LCA Limitations and Future Research

Although LCA software and databases such as GaBi and ecoinvent attempt to consider all production streams and potential variations, capturing all these perfectly is unlikely, especially in the face of future prediction. Since IMA technology is still not in use at an industrial level, this LCA relies on the validity of current datasets to be accurate in the future, a reasonable assumption for most industrial processes but one that can never be fully verified.

Additionally, there is certain knowledge that can be added to this LCA as it becomes available to extend its accuracy. Continued research is needed specifically on possible direct emissions from IMA electrolysis, anode lifetime, and anode recycling processes.

CONCLUSION

Although the Hall–Heroult process has been the only industrial option for aluminum production since the 1890s, inert anodes represent the future of this industry. For this reason, it is crucial to fully understand their effect on the environment and climate.

When electricity production for aluminum electrolysis comes from renewable sources, such as is the case in Iceland, and power requirements for smelting can be limited to 13.5 kWh per kilogram of pure aluminum, IMA offer over a 90% GWP savings from the Hall–Heroult process, as well as over a 30% reduction in PED. At this power requirement, IMA also offer significant GWP savings using global energy data, although this result is cancelled out if power requirements rise to 17 kWh.

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