


Article

Energy and Exergy Analyses of Different Aluminum Reduction Technologies

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Abstract: This paper examines and compares different aluminum reduction technologies found in the literature as alternatives to the current Hall–Heroult technology. The main inefficiencies in the current Hall–Heroult technology were identified and the advantages of the different proposed technologies over the Hall–Heroult technology were determined. The comparison between the different technologies, namely Hall–Heroult, wetted drained cathode, inert anode, and carbothermic, was based on energy and material requirements, and environmental impact. In order to combine all of the evaluation criteria into one numerical value, the exergy concept was utilized as a decision tool. The results emphasize that in order to analyze any conversion system, the exergy of energy, material, environmental impact, and their associated chain production should be taken into consideration.

Keywords: exergy; aluminum; Hall–Heroult; inert anode; wetted drained cathode; carbothermic

1. Introduction

Aluminum's unique properties of low density and corrosion resistance make it a very important metal and a metal of choice to modern manufacturing. The US aluminum industry is the largest industry in the world, processes over 10.7 million metric tons of metal, operates more than 300 plants in 35 states, and employs more than 145,000 people [1]. Unfortunately, aluminum (Al) is one of the most energy-intensive materials to produce, the largest consumer of energy on a per-weight basis, one of the largest contributors to carbon dioxide emissions (CO₂), and the largest electric energy consumer of all industries [2]. However, the aluminum industry has significant opportunities to further reduce its energy intensity and CO₂ emissions. For example, the smelting process in Hall–Heroult technology (the most energy-intensive process in aluminum industry) requires 15.37 kWh/(kg of Al) while the theoretical minimum energy requirement for this process is 6.23 kWh/(kg of Al).

The US Department of Energy Advanced Manufacturing Office has established several roadmaps to pursue research and development in the primary aluminum industry to lower its energy intensity and carbon dioxide emissions [3]. Three attractive technologies have been proposed as alternatives to the current Hall–Heroult smelting technology, namely, the wetted drained cathode, inert anode, and carbothermic methods. However, before implementing these technologies on a commercial basis, they should be justified in terms of energy savings, material resource use, environmental impact, and economical impact (labor, capital investment, and running cost). Unfortunately, no single technology has superiority over the others in all of these criteria; therefore, a decision tool that can combine all of these evaluation criteria into one decision numerical value is very useful for comparing the different technologies in a common base. This can be done by the exergy concept.

Meirbekova et al. [4] investigated the influence of sulfur species in the aluminum smelting process on current efficiency. These authors explored the effect of an increased sulfur concentration in the electrolyte on current efficiency in a laboratory cell. Sodium sulfate was added to the electrolyte as a source of sulfur at regular time intervals to maintain a constant sulfur concentration. The current efficiency decreased by 1.1% for each 100 mg/kg (ppm) increase in sulfur concentration in the electrolyte.

Gunasegaram and Molenaar, [5] used finite element modeling to improve energy efficiency in the electrical connections of Hall–Héroult cells. The authors described two advanced finite element models relating to anode assembly that may be used for designing energy efficient electrical connections. The relative influences of various parameters on the total voltage drop across the anode assembly were quantified and the corresponding effects on energy consumption and greenhouse gas emissions were calculated.

Yang et al. [6], investigated the Inter-Electrode Process of Aluminum Electrolysis. The results showed that the anode–cathode–distance (ACD) consists of three parts: a relatively stable cathode boundary layer, a bubble-free electrolyte layer, and a gas–liquid layer near the anode. The thickness of the aluminum diffusion layer varied with current density, which further determined the critical ACD. The thickness, coverage, and releasing frequency of the bubbles on both laboratory and industrial prebaked cells were derived, and it was found that the average bubble coverage decreased with current density, and the average coverage at 0.8 A cm^{-2} was approximately 50%.

A number of exergy analyses of industrial processes have been conducted [7–12]. Aluminum formation exergy analyses have been conducted [13–15] for several production processes. However, this paper will concentrate on the impact of different primary aluminum production technologies (Hall–Héroult, wetted drained cathode, inert anode, and carbothermic) on energy use, material use, and environmental impact using the concept of exergy.

2. Hall–Héroult Technology

Figure 1 shows a schematic graph of the Hall–Héroult cell that is used currently in primary aluminum production.

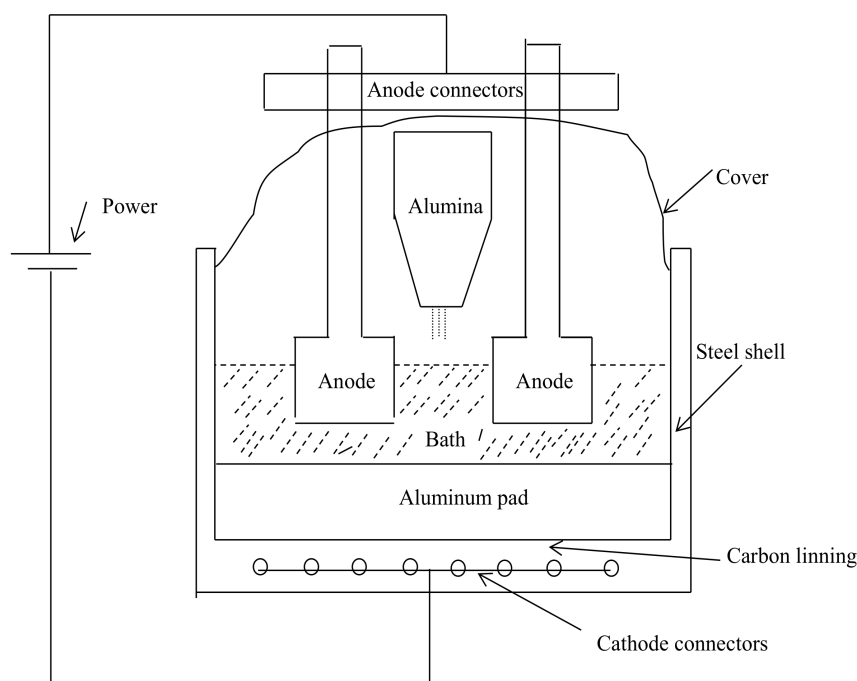


Figure 1. A simple schematic of a Hall–Héroult cell.

The cell consists of the bath (molten cryolite, Na_3AlF_6) in which the alumina (Al_2O_3) is dissolved, and the aluminum is reduced by passing a current through the anode, made mainly from carbon and suspended in the electrolytic bath, to the electrolytic bath, and then to the cathode which consists of molten aluminum contained on a carbon-lined hearth. During the electrolytic reduction, aluminum is deposited in liquid form on the cathode, and oxygen is deposited on the anode. Oxygen reacts with the anode to form CO_2 gas while the aluminum is removed from the cell. The source of alumina is the bauxite ore which consists of alumina in a hydrate form (40–60%), ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), other oxides (silicon and iron), and some minor constituents [16]. Alumina is separated from bauxite by the Bayer process. In this process, bauxite is dissolved in a hot caustic solution to form green liquor which is separated from the undissolved residue and cooled to precipitate pure alumina hydrate. The hydrate is then calcined to produce alumina. The carbon anodes used in aluminum reduction are manufactured from high purity petroleum coke which is ground, calcined, and blended with ground used carbon anodes and pitch that acts as a binder to produce a paste. Two different anode technologies are utilized by US industry, “prebaked” carbon anodes and “in situ baked” Soderberg anodes. Most plants use the prebaked anode, and the plants that use the Soderberg anodes are being replaced by the prebaked carbon anode. For this reason, the analysis will concentrate on the prebaked carbon anodes. The paste is pressed into high-density shapes and baked to carbonize the pitch and to create a solid bond between the particles of calcined coke and used anode material. Sockets are made in the bake anode in which the cast iron is poured to form the electrical connection.

2.1. Main Inefficient Sources of the Current Hall–Heroult Technology

This section introduces the main problems associated with the current Hall–Heroult process and presents the different proposed technologies to overcome these problems.

2.1.1. Carbon Anodes

In the current Hall–Heroult process, the carbon anode is consumed which requires continuous changing. This changing interrupts the production process and results in high carbon dioxide emissions. The reactions occurring at the anode create localized conditions that are different from the bulk of the bath because of the depletion of the supply of reactant and the increased quantity of products (here, the product is carbon dioxide); localized conditions at the anode are unavoidable and require additional energy. To overcome these problems, inert anode technology has been introduced [17] which does not react or dissolve in the cryolite.

2.1.2. Anode–Cathode Distance (ACD)

This is the distance between electrode surfaces, i.e., it is the distance from the lower face of the carbon anode to the top surface of the aluminum pad. This distance is typically about 4 cm to 6 cm [18]. The electrolytic bath occupies the space between the carbon anode and aluminum pad (cathode). The voltage required for the current to pass through the electrolytic is a function of ACD; as the ACD decreases, the voltage (and hence the energy) required decreases. However, the ACD should be kept large enough for the following reasons:

- (a) When current passes through the bath, it creates electromagnetic forces that cause the pad to rotate and deform. If the ACD is small, the molten aluminum pad can reach the anode and make a short circuit; therefore, the ACD is kept large enough to avoid this problem.
- (b) The aluminum reacts with the carbon lining of the cathode and forms aluminum carbide, which dissolves when exposed to electrolyte leaving a corroded cathode surface. Therefore, the aluminum pad rests on a thin sheet of the electrolytic bath, and this creates a gap between the aluminum pad and the carbon cathode (and hence, consumes more energy). To reduce this gap, the aluminum pad and cryolite bath are made to be heavy (and hence, the ACD increases) to tightly compress them together.

By better designing the cathode surface to make it more wettable and inert to the aluminum pad, a better contact can be achieved between the aluminum pad and the cathode surface. If this happens, the ACD can be reduced, thus decreasing the voltage drop and hence, resulting in energy saving. The wetted drained cathode provides these properties [18]. The cathode is made from a wettable cathodic material (like TiB_2), and it is designed in such a way to allow the aluminum to be drained, leaving a very thin layer of aluminum. The configuration of this technology is shown in Figure 2.

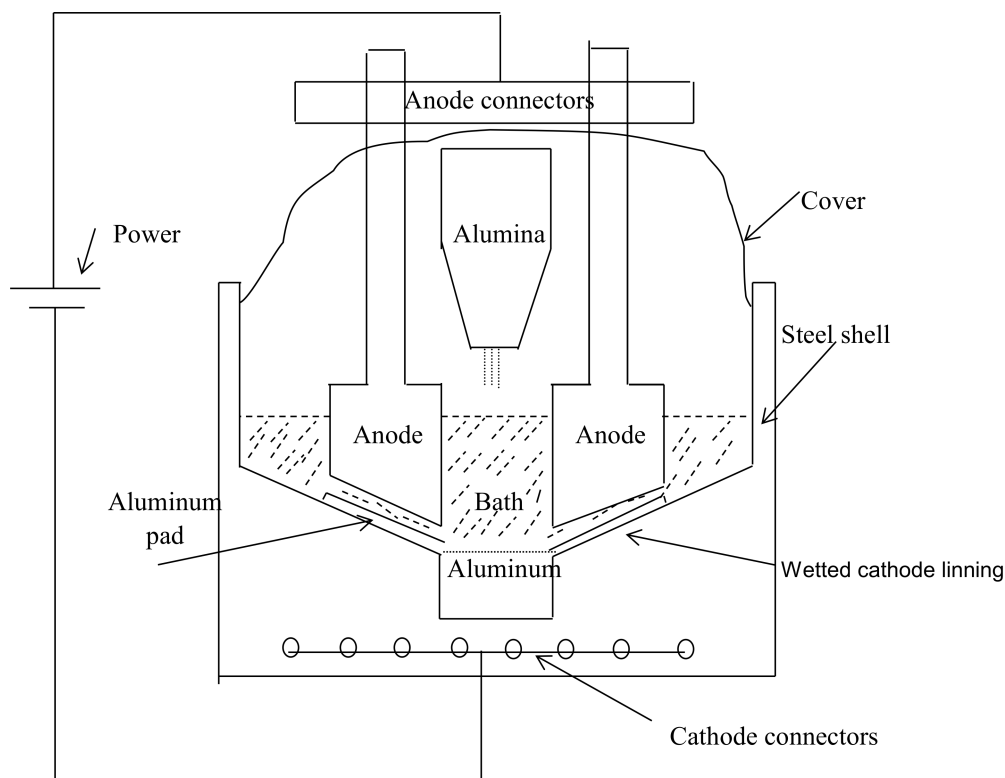


Figure 2. Wetted drained cathode cell.

2.1.3. High Voltage

The energy consumed in the electrolytic reaction is a function of the voltage used and the current's efficiency. The distribution of the voltage components is shown in Table 1 [19]. Since the typical current efficiency of Hall–Heroult technology is 90%, attention should be paid to reduce the voltages of Hall–Heroult components.

Table 1. Voltage components for the electrolytic reduction cell.

Component	Voltage (V)	Distribution (%)
External connections	0.16	3.4
Anode	0.32	6.9
Polarization	0.60	12.9
Bath	1.76	38.0
Reaction	1.20	25.9
Cathode	0.47	10.1
Other	0.13	2.8

As shown from this table, most of the energy is consumed to overcome the resistances of cell components. For this reason, the carbothermic reduction process that is non-electrochemical has been suggested.

3. Analyses

3.1. Theoretical Energy

Material uses and environmental impact of the different primary aluminum production processes. Only the consumable materials have been considered. As an example, the cryolite used in the bath has not been considered in the analysis since it is not consumable during the reduction (or lost in a very small portion). Only carbon dioxide emissions (and the carbon monoxide for the carbothermic process) have been considered since they represent the majority of reduction process emissions.

3.1.1. Hall–Heroult Process

In order to estimate the theoretical energy requirements, the conservation of energy should be applied to the reacting systems. The net reaction for the carbon anode Hall–Heroult process is shown in Figure 3 and summarized in Equation (1):

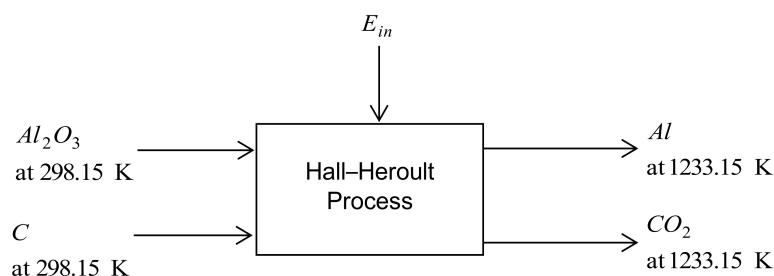
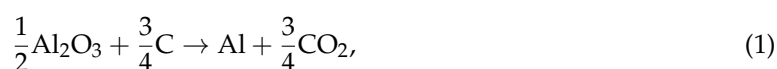


Figure 3. Aluminum reduction in the Hall–Heroult process. The output products are assumed to have the same temperature as the reduction temperature of 960 °C [19].

Apply the first law energy conservation principles (assuming no heat losses),

$$E_{in} = \sum_o (n_o \times \bar{h}_o) - \sum_i (n_i \times \bar{h}_i) \quad (2)$$

where E_{in} is the electricity input to the process, \bar{h}_o is the enthalpy of formation of element output o , \bar{h}_i is the enthalpy for the formation of element input i , n_o is the number of moles of element output o , and n_i is the number of moles of element input i . Table 2 presents the values of enthalpy of formation of the compounds that will be used in this paper [20], and these values are substituted into Equation (2):

$$\begin{aligned} E_{in} &= (1 \times 0 + \frac{3}{4} \times -393.52 - \frac{1}{2} \times -1675.69 - \frac{3}{4} \times 0) \\ &= 542.71 \frac{\text{kJ}}{\text{mole of Al}} = 20,100 \frac{\text{kJ}}{\text{kg of Al}} = 5.59 \frac{\text{kWh}}{\text{kg of Al}} \end{aligned}$$

Table 2. Selected values of enthalpy of formation at ambient temperature.

Substance	Enthalpy of Formation (MJ/kmol)	Enthalpy of Formation (MJ/kg)
Al ₂ O ₃	−1675.690	−16.428
CO ₂	−393.520	−8.944
CO	−110.530	−3.948
O ₂	0	0
C	0	0

The above calculations assume that the aluminum and carbon dioxide exit at the ambient temperature (the enthalpies of formation are estimated at ambient temperature); however, it is assumed that the reaction products exit at the reaction temperature (assumed to be 1233.15 K). The energy required to change the temperature of these substances is calculated from their heat capacities. The following equation can be used to estimate the energy required:

$$\text{Energy required to change temperature} = \int_{T_0}^T cp(T)dT \quad (3)$$

where $cp(T)$ is the heat capacity to the ambient temperature, assumed to be 298.15 K, and T is the exit temperature, assumed to be 1233.15 K. Tables 3 and 4 [21,22] show the variation in heat capacity with temperature for aluminum and some gases (assuming ideal gas), respectively.

Table 3. Variation in heat capacity with temperature for aluminum *.

Temperature Range (K)	A	B	C	D	E
<933.45	6.71348	−1.29418	2.04599	0.81916	−0.066294
>933.45	7.58868	9.40685×10^{-9}	4.26987×10^{-9}	6.43922×10^{-9}	1.30976×10^{-9}

* cp (kJ/mole K) = $0.004184 (A + B t + C t^2 + D t^3 + E/t^2)$, $t = T/1000$, T in K.

Table 4. Variation of heat capacity with temperature for some gases *.

Substance	α	$\beta \times 10^{-3}$	$\gamma \times 10^{-6}$	$\delta \times 10^{-9}$	$\epsilon \times 10^{-12}$
CO	3.710	−1.619	3.692	−2.032	0.240
CO ₂	2.401	8.735	−6.607	2.002	0
O ₂	3.626	−1.878	7.055	−6.764	2.156

*: cp (kJ/mole K) = $R \times (\alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4)$ T in K.

By applying Equation (3), the energy levels required to change the temperature from 298.15 K to 1233.15 K for the aluminum and carbon dioxide were found to be 0.284 kWh/(kg of Al) and 0.358 kWh/(kg of Al), respectively. All values were calculated corresponding to 1 kg of aluminum. Therefore, the total theoretical minimum energy requirement for the Hall–Heroult process is 5.59 kWh + 0.284 kWh + 0.358 kWh = 6.232 kWh/(kg of Al).

Theoretically, from Equation (1), $\frac{1}{2}$ kmol of alumina and $\frac{3}{4}$ kmol of carbon are consumed, respectively, in order to produce 1 kmol of aluminum. These values are equivalent to 1.89 kg of alumina and 0.33 kg of carbon per 1 kg of aluminum (using the molecular mass values from Table 5). Also, the reduction is associated with $\frac{3}{4}$ kmol of carbon dioxide for each 1 kmol of aluminum produced, which corresponds to 1.22 kg of CO₂ per 1 kg of aluminum.

Table 5. Standard chemical exergy of selected substances.

Substance	Molecular Mass (kg/kmol)	Gibbs Free Energy (kJ/kmol)	Standard Chemical Exergy (kJ/kmol)	Standard Chemical Exergy (kJ/kg)
O ₂	32	0	3924	123
CO ₂	44	−394,380	19,817	450
C	12	0	410,272	34,189
Al	27	0	888,746	32,917
Al ₂ O ₃	102	−1,581,000	202,380	1984
CO	28	−137,020	275,214	9829
SiO ₂	60	−856,000	1900	32
Si	28	0	853,977	30,499
Al ₂ O ₃ ·3H ₂ O	156	−2,287,400	227,267	1456
Al ₂ SiO ₅	162	−2,625,880	15,400	95
H ₂	2	−236,100	236,100	118,050

3.1.2. Inert Anode Hall–Heroult

This process is summarized in Figure 4 and Equation (4),

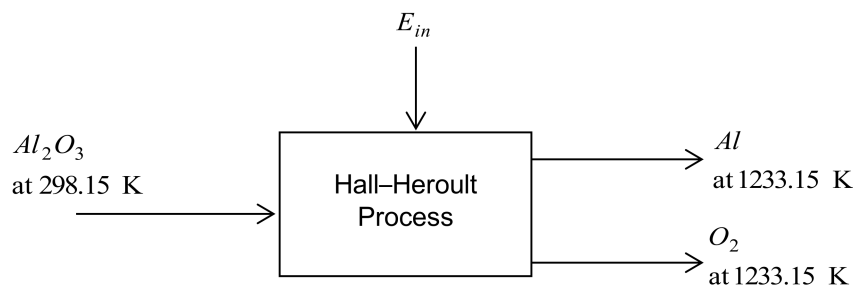


Figure 4. Inert anode Hall–Heroult process.

Apply Equation (2) to estimate the minimum energy requirement,

$$\begin{aligned} E_{in} &= \left(1 \times 0 + \frac{3}{4} \times 0 - \frac{1}{2} \times -1675.69 \right) \\ &= 837.85 \frac{\text{kJ}}{\text{mole of Al}} = 31,031 \frac{\text{kJ}}{\text{kg of Al}} = 8.63 \frac{\text{kWh}}{\text{kg of Al}} \end{aligned}$$

As discussed before, additional energy is required to change the temperatures of aluminum and O_2 (in this case) from ambient to operating temperatures. The energy requirement for aluminum is the same as calculated before; however, the energy required for the temperature change in O_2 can be calculated in the same manner; this results in 0.27 kWh/(kg of Al). The total theoretical energy requirement is $8.63 + 0.284 + 0.27 = 9.184$ kWh/(kg of Al).

This technology requires the same theoretical quantity of alumina; however, no carbon is consumed in this process and hence, there are no carbon dioxide emissions.

3.1.3. Wetted Drained Cathode

The same general setup as the Hall–Heroult process is used here, but the geometry and type of cathode are changed and modified to decrease the ACD. Therefore, the theoretical energy requirement, and the quantities of alumina, carbon, and carbon emissions are same as for the conventional Hall–Heroult process, but the actual energy requirement will be decreased due to the ACD decrease as described later, in Section 3.2.3.

3.1.4. Carbothermic Technology

This process is a two-stage process taken place in a reactor at a temperature of ~ 2000 °C [23]. In the first stage, the alumina is allowed to react with the carbon to form aluminum carbide and carbon monoxide, while, in the second stage, the aluminum carbide is recovered and allowed to react with alumina to form aluminum and carbon monoxide. Efficient recovery of the aluminum carbide is necessary to make this process economically viable [23]. The net reaction for the carbothermic technology is summarized in Figure 5 and Equation (5).



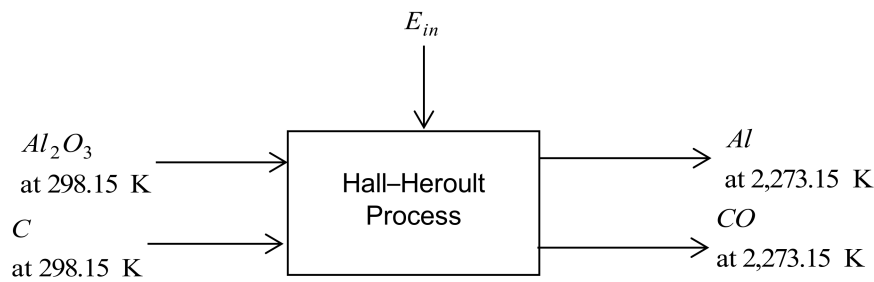


Figure 5. Carbothermic reduction process.

The minimum energy requirement is calculated using Equation (2),

$$\begin{aligned}
 E_{in} &= \left(1 \times 0 + \frac{3}{2} \times -110.53 - \frac{1}{2} \times -1675.69 - \frac{3}{2} \times 0 \right) \\
 &= 672.1 \frac{\text{kJ}}{\text{mole of Al}} = 24,891 \frac{\text{kJ}}{\text{kg of Al}} = 6.92 \frac{\text{kWh}}{\text{kg of Al}}
 \end{aligned}$$

The energy required to change the temperature of aluminum from 298.15 K to 2273.15 K is calculated using Equation (3); this results in a value of 0.623 kWh/(kg of Al). The energy required for the carbon monoxide temperature change can be calculated in the same manner; this results in a value of 0.58 kWh/(kg of Al). The total minimum energy requirement is $6.92 + 0.623 + 0.58 = 8.123$ kWh/(kg of Al).

The theoretical quantities of alumina and carbon are 1.89 kg/(kg of Al) and 0.67 kg/(kg of Al), respectively (from Equation (5)). The theoretical carbon monoxide emission is 1.56 kg/(kg of Al) (from Equation (5)).

3.2. Actual Energy Consumption, Material Uses and Environmental Impacts of the Different Primary Aluminum Production Processes

3.2.1. Hall-Heroult Process

The actual electrical consumption of the Hall-Heroult reduction process, EC , can be determined by the following relation [16]:

$$EC(\text{kWh/kg of Al}) = 298.06 \times E_{cell} / CE \quad (6)$$

where E_{cell} is the total voltage per cell, Volts, and CE is the current efficiency (%). The typical total voltage for the current Hall-Heroult cells is 4.64 V [22] and the typical current efficiency is 90% [24]. Therefore, the typical electrical consumption of the current Hall-Heroult cell is 15.37 kWh/(kg of Al). The current cell efficiency, $\eta_{Hall-Heroult}$, can be estimated as

$$\eta_{Hall-Heroult} = \frac{\text{Theoretical electrical requirement}}{\text{Actual electrical requirement}} = \frac{6.23}{15.37} = 40.5\%. \quad (7)$$

In practice, 1.93 kg of alumina is required for each 1 kg of aluminum. The excess amount is either lost or used to capture the Hydrogen fluoride (HF) gases that result from the reduction of aluminum [19]. Two main sources are responsible for the CO₂ emission from the reduction process: the reduction reaction (as shown by Equation (1)) and carbon anode oxidation (due to high operating temperature). As shown previously, theoretically, 0.33 kg of carbon anode is consumed to produce 1 kg of aluminum; however, 0.45 kg of carbon anode is consumed in the actual process [16]. Most of the excess carbon is oxidized from the high-temperature anode surface, and some excess carbon is used to protect the iron electrical connections in the anode. The excess carbon is assumed to be fully oxidized:



One kmol of CO₂ (44 kg) is produced from the oxidation of 1 kmol of carbon (12 kg), and 0.12 kg of carbon will produce 0.44 kg of CO₂.

Therefore, the actual CO₂ emissions sum to 1.66 kg/(kg of Al).

3.2.2. Inert Anode Technology

Carbon anodes are consumed in the conventional Hall–Heroult process; however, introducing inert anodes into the Hall–Heroult process will eliminate the problem of consumable anodes. The material of the inert anodes must be highly conductive and thermally and mechanically stable at 960 °C (materials such as ceramics, cermets, and metals). As discussed before, the reactions occurring at the anode create localized conditions which add an additional 0.6 V to the overall cell voltage (from Table 1). Since there are no reactions at the inert anode, the polarization voltage can be reduced to 0.15 V [17].

In the conventional Hall–Heroult cell, the energy required by the cell is partly provided by oxidation of the carbon anode; this is not the case for inert anodes. As shown before, the theoretical energy requirement for an inert anode is higher than that for the conventional Hall–Heroult process by 2.95 kWh/(kg of Al). The inert anode must supply the full minimum energy requirement for alumina reduction; therefore, the voltage required should be increased by 0.89 V (from Equation (6)).

Combining both effects (reduced polarization and increased reaction voltage) will result in a voltage increase of 0.44 V voltage. The total voltage required for the inert anode technology is then 5.08 V which corresponds to 16.82 kWh/(kg of Al) (from Equation (6)).

Since no changes to the alumina feeding system occur, the actual alumina consumption is assumed to be the same as for the conventional Hall–Heroult process. However, no carbon anode is consumed, and hence, no carbon dioxide emission is emitted in this technology.

3.2.3. Wetted Drained Cathode Technology

Decreasing the ACD results in a proportional decrease in the voltage drop associated with the electrolytic bath. In conventional Hall–Heroult technology, the voltage drop through the bath is 1.76 V (as shown in Table 1), and this is due to a typical 5 cm of ACD; however, the ACD can be lowered to 2 cm for the wetted drained technology [15]. The voltage drop will be decreased in a proportional way to 0.704 V [15]. The total voltage drop will accordingly be reduced to 3.58 V (compared to 4.64 V in conventional Hall–Heroult process), i.e., a reduction of 23% in electrical energy usage. As discussed before, the current average electrical consumption is 15.37 kWh/(kg of Al); with the 23% reduction in electrical usage, the wetted drained cathode technology will consume only 11.83 kWh/(kg of Al).

Since no changes occur to the alumina feeding system or the anode, the actual alumina, anode consumption and carbon dioxide emissions are assumed to be the same as for the conventional Hall–Heroult process.

3.2.4. Carbothermic Technology

This technology is a non-electrolytic process that produces aluminum using a chemical reaction that takes place within a reactor. The process is a multi-step chemical reaction process with a net reaction as shown before. The reactor can be designed to provide a thermal efficiency of 80% [23]. Therefore, the actual energy requirement can be estimated as:

$$\eta_{\text{carbothermic}} = \frac{\text{Theoretical electrical requirement}}{\text{Actual electrical requirement}} = \frac{8.123}{\text{Actual electrical requirement}} = 80\% \quad (9)$$

So, the actual electrical requirement is 10.15 kWh/(kg of Al).

By using an efficient recovery system, the actual alumina and carbon consumption are almost as same as the theoretical values [23].

3.3. Summary

Table 6 summarizes the actual energy, material uses, and environmental impacts of the previously described technologies.

Table 6. Results summary of the different aluminum reduction technologies (per 1 kg of Al).

Technology	Energy Use (kWh)	Alumina (kg)	Carbon Anode [carbon] (kg)	CO ₂ (kg) [CO] (kg)
Hall–Heroult	15.37	1.93	0.45	1.66
Wetted cathode	11.83	1.93	0.45	1.66
Inert anode	16.82	1.93	0	0
Carbothermic	10.15	1.89	[0.67]	[1.56]
Best technology	Carbothermic	Carbothermic	Inert anode	Inert anode

As can be seen from this table, each criterion decision (energy use, material use, and environmental impact) gives a different picture of which technology that should be adopted. A decision tool that can combine all these evaluation criteria in one decision numerical value would be very useful for comparing the different technologies on a common basis. This can be achieved through the exergy concept, as described below.

4. Using Exergy as a Decision Tool

Exergy is the maximum amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium (thermal, mechanical and chemical equilibrium) with the common components of the natural environment by means of reversible processes. Here, the matter refers to any substance (fuel, material, emissions, etc.). This makes exergy a more natural choice for a common measure of different matters; hence, it has been suggested that exergy is the most suitable indicator for both resource and waste accounting as it enables the analyst to evaluate and compare all inputs and outputs on a common basis, and it is believed that exergy should be used as a quantifier when different matters need to be compared against each other [25–27]. The subsequent analysis will use exergy for the following aspects [28]:

- As a measure of natural resource use—natural resources are traditionally divided into fuels and other (ex. material) resources. This division seems arbitrary; oil is usually considered to be a fuel resource and wood, a construction material. However, oil can be used for producing useful materials and wood can be used as a fuel. Therefore, it would be more appropriate to treat these resources together; the exergy concept can be used in this situation.
- As a measure of the resources needed to clean the emissions. Since pollution is due to the change in concentration of some specific substances in the environment, the exergy required in a process to remove a number of the substances which are released by a system can be considered as the measure of the environmental impact caused by this system.
- As a comparison criterion by combining the two above uses to measure how effective and environmentally-friendly a primary aluminum technology is regarding natural resources.

It is relatively easy to define the appropriate level of pressure and temperature for the environment. This is not the case for the calculation of chemical exergy, which requires knowledge of the detailed average chemical composition of the substances under consideration and the environment in which the substances interact. Therefore, this section will start by defining the chemical environmental conditions that are used in this paper, followed by the techniques used to calculate the exergy of different matters.

4.1. The Reference Environment

In order to calculate the chemical exergy, the environment, which is in a stable equilibrium and has a unique temperature (T_0), pressure (P_0), and chemical compositions for the components making it

up, should be defined first. All substances of interest should be formable from the substances making up the environment. In this paper, the dead state proposed by [29] was used. In this model, three main sinks—atmosphere, oceans, and crust—were considered, and the following dead states have been suggested [29]:

1. For gaseous substances, such as O₂, N₂, CO₂, H₂O, D₂O, Ar, He, Ne, Kr and Xe, a standard atmosphere, shown in Table 7, can be used to represent the dead states of these gases.

Table 7. The composition of gaseous reference substances in the standard atmosphere.

Substances	Conventional Mean Pressure in the Environment (kPa *)
Ar	0.906
CO ₂	0.0335
D ₂ O (g)	0.000342
H ₂ O (g)	2.2
He	0.000485
Kr	0.000097
N ₂	75.78
Ne	0.00177
O ₂	20.39
Xe	0.0000087

* The mean atmospheric pressure is 99.31 kPa.

2. For substances such as Al, Co, Cr, Fe, Mg, Mn, P, Sb and Si, a standard Earth's land surface, shown in Table 8, is adopted to represent the dead states of these elements.

Table 8. The conventional average concentration of selected solid reference species in the external layer of the Earth's crust.

Chemical Element	Reference Species	
	Formula	Mole Fraction
Al (s)	Al ₂ SiO ₅	2×10^{-3}
Co (s)	Co ₃ O ₄	2×10^{-7}
Cr (s)	Cr ₂ O ₃	4×10^{-7}
Fe (s)	Fe ₂ O ₃	1.3×10^{-3}
Mg (s)	CaCO ₃ OMgCO ₃	2.3×10^{-3}
Mn (s)	MnO ₂	2×10^{-4}
P (s)	Ca(PO ₄) ₂	4×10^{-4}
Si (s)	SiO ₂	0.472

3. For substances that exist as ions in the water, the composition of the ions or compounds as existing in standard seawater is adopted, as shown in Table 9.

Table 9. Selected reference species dissolved in seawater.

Chemical Element	Reference Species	
	Chemical Formula	Average Molarities (mole/kg H ₂ O)
Ca (s)	Ca ²⁺	9.6×10^{-3}
Cl ₂ (g)	Cl ⁻¹	0.5657
Cu (s)	Cu ²⁺	7.3×10^{-10}
F ₂ (g)	F ⁻¹ⁱ	3.87×10^{-5}
Na (s)	Na ⁺	0.474

4.2. Exergy Calculations

Based on the dead states discussed above, the following equations can be used to calculate the chemical exergies of different substances.

1. For the reference substances that exist in the atmosphere air, and assuming ideal gas behaviors, the chemical exergy is given by [30]:

$$EX_{ch,i} = RT_0 \ln \frac{P_i}{P_{o,i}} \quad (10)$$

where $EX_{ch,i}$ is the chemical exergy of substance i that exists in the atmospheric air, P_i and $P_{o,i}$ are the partial pressures of substance i in the stream under consideration and in the dead state, respectively, and R is the universal gas (8.314 kJ/kmol K).

2. Only 10 chemical elements can be defined using the reference atmosphere; however, for other elements, the Earth's surface and seawater can serve as the dead states. In such situations, chemical exergy can be calculated by the following equation [30]:

$$EX_{ch} = \Delta_f G^0 + \sum_i (n_i \times EX_{ch,i}) \quad (11)$$

where $\Delta_f G^0$ is the standard normal free energy of formation, n_i is the number of moles of element i in the compound under consideration, and $EX_{ch,i}$ is the chemical exergy of element i of the compound. Table 5 presents the selected standard normal free energy of formation for some compounds used in this thesis [20]. Using Equations (10) and (11) and assuming the temperature, T , and pressure, P , of the stream, are equal to those of the dead state, i.e., T_0 and P_0 ($P_0 = 1$ atm and $T_0 = 298.15$ K), and all gases under consideration are treated as ideal gases, Table 5 summarizes the standard chemical exergy of the substances that will be used in this paper.

4.3. Proposed Exergy Model

A general aluminum production flow process is illustrated in Figure 6. The process has input streams flowing in (direct energy and material inputs) and output streams (aluminum, waste losses, and emissions to the environment). The traditional energy analysis of this process considers only the direct energy consumption and tries, by any means, to reduce it for a given unit of useful output (aluminum). However, the complete analysis should also include the uses of other natural resources as well as the environmental impact.

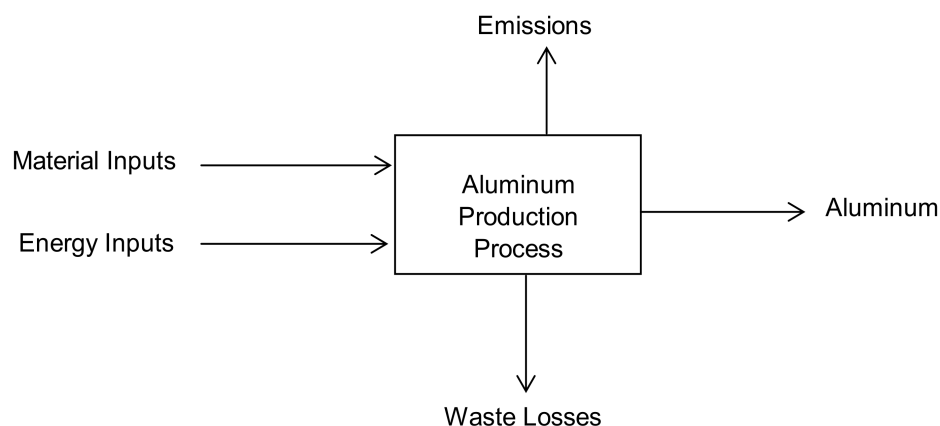


Figure 6. Illustration of the primary aluminum process.

As discussed before, in order to compare the different inputs and outputs on an equivalent basis, the inputs and outputs need to be expressed as their equivalent exergies. Also, the direct exergy components (energy and material) require exergy during their chain productions to achieve their final states. In addition, the impact of some emissions (like carbon dioxide, carbon monoxide, etc.) on the environment should be considered in the complete analysis. To include the impact of these emissions on the environment, the emissions are assumed to be cleaned first before their delivery to the environment; this cleaning requires additional exergy. Therefore, when the aluminum process is analyzed completely, it is necessary to consider the direct exergy of the energy and material consumption, the exergy consumed in chain production, and the exergy needed for cleaning purposes during chain production.

Figure 7 shows the proposed exergy flow model for the analysis of the primary aluminum production process. In this model, the exergy of the fuel resources, EX_{FR} , is first processed into its useful exergy, EX_{EU} , which acts as the input to the material processing (to process the material resource exergy, EX_{MR} , into its useful exergy, EX_{MU}), EX_{EM} , the primary aluminum process, EX_{EP} , cleaning processing, EX_{EC} , and for the fuel processing itself, EX_{EF} . If the pollution stream is required to have a zero impact on the environment (or any other level), the stream should undergo a cleaning recovery process to bring it to the cleaning level, $EX_{em,C}$. The cleaning recovery system is used to clean up the total exergy pollution stream from the processing of fuel resources, $EX_{em,F}$, the primary aluminum production, $EX_{em,P}$, and from the material processing, $EX_{em,M}$. Note that EX_{LF} , EX_{LM} , EX_{LC} , and EX_{LP} represent the exergy waste in fuel processing, material processing, the cleaning process, and primary aluminum production, respectively. The summation of $EX_{em,i}$ and $EX_{L,i}$ over all processes of i (fuel processing, material processing, primary aluminum production, etc.) within the chain production represents the total exergy loss (but not destruction). EX_U represents the exergy of the useful output of the primary aluminum production (here, it is the aluminum).

As shown clearly from this figure, the use of different technologies for primary aluminum production impact not only the direct exergy consumption of primary aluminum production, E_{EP} , and E_{MU} , but also the exergy needed for production, E_{EF} and E_{EM} , and the exergy required to clean up the environmental impact, E_{EC} . The purpose of the analyses here is to compare the different primary aluminum production technologies against each other to *optimize* the overall energetic efficiency, $E_U/(\text{total exergy spent during the chain production})$. This expression is compatible with the thermo-economic analysis, except that exergy is used as quantifier of energetic and non-energetic exchanges, instead of money, since exergy is a measure of the usefulness of specific matter to the environment [31].

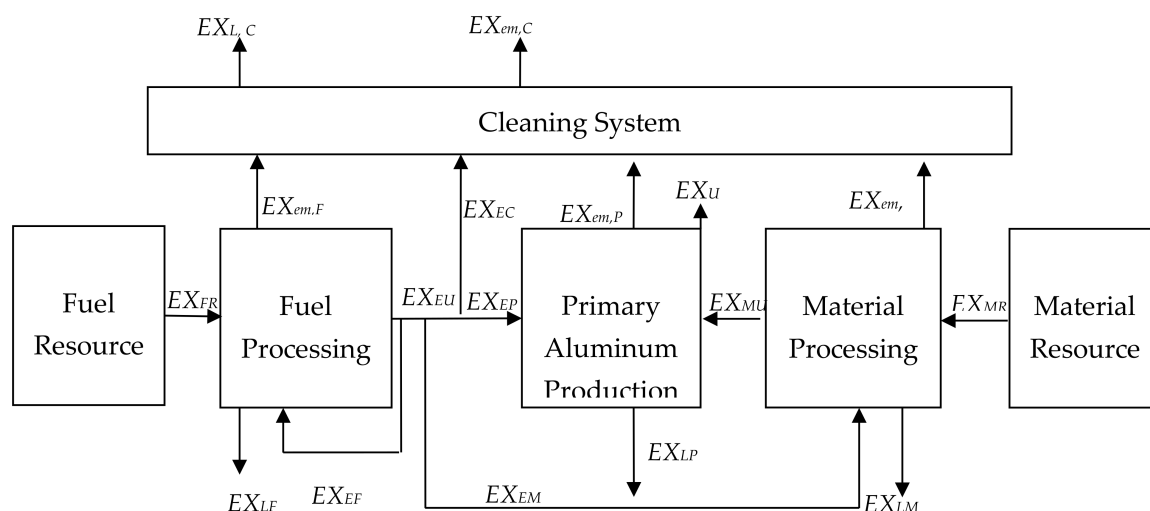


Figure 7. The proposed exergy flow diagram for the primary aluminum process.

5. Results and Discussion

5.1. Source Fuel Exergy

Fuel can be divided into two groups: primary and secondary. A primary fuel can be used without any modification to its chemical structure, such as coal, oil, natural gas, etc. A secondary fuel is an energy which has been derived from a primary fuel, such as electricity, gasoline, etc.

The source exergy of any fuel, $EX_{fuel,S}$, includes the exergy content of the fuel (direct exergy, $EX_{fuel,C}$) and the exergy used throughout the processing sequences, from the extraction of the fuel in the fuel reservoir to its delivery to the system (production exergy, $EX_{fuel,P}$). The exergy content of the fuel is the work obtainable when the fuel is brought from its current state to the dead state. For electricity, this is exactly equal to the electrical energy, while for a pure chemical fuel, this can be calculated by Equation (11), presented before. Equation (11) can be used to calculate the exergy content (direct exergy) for a variety of fuels when the chemical composition of the fuel is known. The exergy efficiency of the fuel, $\psi_{EX,f}$, can be defined as [28]:

$$\psi_{EX,f} = \frac{\text{Exergy available in the final product}}{\text{Total input exergy}} \quad (12)$$

For the primary fuel,

$$\psi_{EX,f} = \frac{EX_{fuel,C}}{EX_{fuel,S}} = \frac{EX_{fuel,C}}{(EX_{fuel,C} + EX_{fuel,P})} \quad (13)$$

Table 10 presents a set of values for sources of exergy associated with selected fuels; these values were compiled from different sources [29,32–34].

Table 10. Typical values for production exergy, content exergy, and exergitic efficiencies for different fuels.

Fuel (1 kg)	Production and Delivery Exergy (MJ)	Exergy Content of Fuel (MJ)	Source Exergy (MJ)	Exergy Efficiency (%)
Coal	1.4	34.2	35.6	96.1
Coke	4.0	29.9	33.9	88.2
Natural gas	7.1	51.8	58.9	87.9
Fuel oil	8.9	47.1	56.0	84.1
Kerosene	8.9	46.5	55.4	83.9
Diesel	8.8	44.4	53.2	83.5
Gasoline	9.7	47.5	57.2	83.0
Propane	8.9	48.8	57.7	84.6
Butane	8.9	48.3	57.2	84.4
Calcined petroleum coke	0.4	35.4	35.8	98.9
Pitch	0.04	40.2	40.2	99.9
Green coke	0.5	33.0	33.5	98.5

For the secondary fuel, there may be several processes during the fuel production. In such instances, the production exergy of the fuel is composed of several terms [28]:

$$EX_{fuel,P} = \sum_i (EX_{fuel,P_i}), \quad (14)$$

and the exergy efficiency becomes:

$$\psi_{EX,f} = \frac{EX_{fuel,C}}{(EX_{fuel,C} + EX_{fuel,P_1} + EX_{fuel,P_2} + \dots)}. \quad (15)$$

As an example, the electricity exergy efficiency can be estimated as follows. Figure 8 shows a general electricity production chain process:

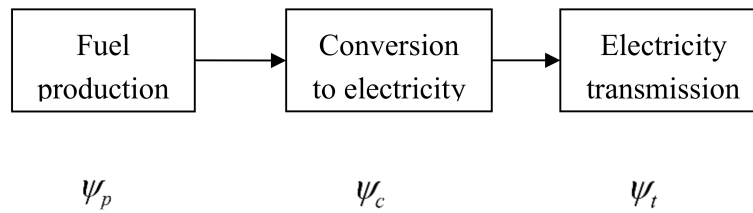


Figure 8. Electricity production chain process.

where ψ_p is the exergy efficiency of the fuel production, ψ_c is the electricity conversion exergy efficiency, and ψ_t is the electricity transmission exergy efficiency. It is assumed that 50% of the electricity used in the primary aluminum smelting process comes from a hydroelectricity source, and the remaining 50% comes from the different mixed fuel sources [35]. The overall exergy efficiency of the electricity production for a specific source, $\psi_{o,i}$, can be estimated as:

$$\psi_{o,i} = \psi_p \times \psi_c \times \psi_t. \quad (16)$$

The overall weighted electricity exergy efficiency of the US from the different fuel sources was estimated by the Energy Information Administration (EIA) as 33% [36]. This efficiency will be assumed for the electricity produced from different fuel sources in the smelting process. Assuming the following efficiencies for the hydroelectric source [37] are

$\psi_p = 1$, $\psi_c = 0.830$, and $\psi_t = 0.864$, the overall exergy efficiency for the hydroelectric source, $\psi_{o,hydro}$, is

$$\psi_{o,hydro} = 1 \times 0.83 \times 0.864 = 0.72.$$

The weighted average exergy efficiency of electricity used for the smelting process ψ_o is

$$\psi_o = 0.5 \times 0.33 + 0.5 \times 0.72 = 0.525. \quad (17)$$

The production exergy used in electricity generation, $EX_{ele,p}$, (the exergy spent to produce 1 kWh of electricity) of the electricity can be evaluated as

$$\begin{aligned} EX_{ele,p} &= EX_{ele,C} / \psi_o - EX_{ele,C} = 3412 / 0.525 - 3412 = 3087 \text{ Btu/kWh} \\ &= 3241 \text{ kJ/kWh} \end{aligned} \quad (18)$$

where $EX_{ele,C}$ is the exergy content of 1 kWh (3412 Btu/kWh). The source exergy of 6499 Btu/kWh (6824 kJ/kWh) will be used for electricity consumed in the anode and smelting processes (both processes are within the primary aluminum industry), while a source exergy of 10,250 Btu/kWh (10,763 kJ/kWh) will be used for the alumina production since this process occurs outside the primary aluminum industry. The source exergy of the electricity is the summation of the production exergy and the exergy content of the electricity,

$$EX_{ele,S} = EX_{ele,C} + EX_{ele,p} = 3412 + 3087 = 6499 \text{ Btu/kWh} = 6824 \text{ kJ/kWh}. \quad (19)$$

5.2. Material Source Exergy

The direct exergy content of different materials used in the primary aluminum production has been calculated before. This section will estimate the source exergies of these materials. The source exergy of a material includes the exergy content of the raw material augmented by the sum of all the net exergetic inputs received during the production process of the raw material [32].

5.2.1. Alumina

The US refines bauxite to produce 53% of alumina required, and the other 47% is imported [35]. The analysis in this paper is concerned with the processes carried out within the US. So, the exergy of imported alumina will take the value of direct exergy content as estimated previously (1.984 MJ/kg or 1880 Btu/kg). All commercial alumina in the US is refined from imported bauxite (mainly contains gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) using the Bayer refining process. The main energy and material inputs for this process are shown in Table 11 [35].

Table 11. Energy and material inputs for alumina refining (per 1 kg of alumina).

Natural Resource	Quantity
Fuel oil (kg)	0.093
Natural gas (kg)	0.17
Electricity (kWh)	0.109
Bauxite (kg)	2.64

The source exergy can be estimated (utilizing the exergy content and production exergy as estimated before) as

$$EX_{alumina} = 2.64 \text{ kg} \times 1456 \frac{\text{kJ}}{\text{kg}} + 0.093 \text{ kg} \times 56,000 \frac{\text{kJ}}{\text{kg}} + 0.17 \text{ kg} \times 58,900 \frac{\text{kJ}}{\text{kg}} + 0.109 \text{ kWh} \times 10,763 \frac{\text{kJ}}{\text{kWh}} = 20,238 \frac{\text{kJ}}{\text{kg of alumina}} \quad (20)$$

The weighted source exergy of alumina (imported and produced alumina) is estimated as $0.53 \times 20,238 \text{ (kJ/kg)} + 0.47 \times 1984 \text{ (kJ/kg)} = 11,659 \text{ kJ/(kg of alumina)}$.

5.2.2. Carbon Anode

The main energy and material inputs required to produce 1 kg of carbon anode are shown in Table 12 [35].

Table 12. Energy and material inputs for carbon anode production.

Natural Resource	Quantity
Fuel oil (kg)	0.004
Natural gas (kg)	0.073
Electricity (kWh)	0.266
Caclined petroleum coke (kg)	0.82
Pitch (kg)	0.231
Green coke (kg)	0.085

The source exergy of the carbon anode can be estimated as

$$EX_{carbon \text{ anode}} = 0.004 \text{ kg} \times 56,000 \frac{\text{kJ}}{\text{kg}} + 0.073 \text{ kg} \times 58,900 \frac{\text{kJ}}{\text{kg}} + 0.266 \text{ kWh} \times 6824 \frac{\text{kJ}}{\text{kWh}} + 0.82 \text{ kg} \times 35,800 \frac{\text{kJ}}{\text{kg}} + 0.231 \text{ kg} \times 40,240 \frac{\text{kJ}}{\text{kg}} + 0.085 \text{ kg} \times 33,500 \frac{\text{kJ}}{\text{kg}} = 47,838 \frac{\text{kJ}}{\text{kg of carbon anode}} \quad (21)$$

Unlike a carbon anode, the carbon used in carbothermic technology does not require the exergy associated with the carbon anode manufacturing. Hence, only the source exergy of the calcined petroleum will be used for the carbon consumed in carbothermic technology (35,800 kJ/kg).

5.3. Source Exergy of the Environmental Impact

The primary aluminum industry participated in many of Environmental Protection Agency's programs to reduce its emission impact on the environment. As an example, in 1994, the industry spent nearly \$20 million on capital expenditure for pollution control, on top of more than \$32 million the previous year [38]. Any future regulations will greatly impact the primary aluminum industry.

The heavy consumption of the material and fuel resources in the current primary aluminum technology causes environmental problems. One of these problems is the global warming resulting from the heavy emissions of carbon dioxide. These emissions change the concentrations of certain gases in the atmosphere which, in turn, influence global warming. As discussed before, the methods and techniques for analyzing, improving and optimizing the primary aluminum production process have to deal not only with direct fuel exergy consumption, but also with other resources which have associated exergy consumption, and with environmental impact.

The chemical exergy of the emission of any industrial process can be used as a preliminary tool for the evaluation of environmental impact, as it gives an indication of how far the substance is from equilibrium with the common state of the environment [25,31]. In this sense, a high exergy content is a simple indication that the substance under consideration is likely to drive further chemical reactions when it is discharged to the atmosphere. As an example, carbon monoxide has higher chemical exergy than carbon dioxide (as shown in Table 5) and it is also known to have a higher environmental impact.

Due to the lack of information regarding the actual exergy required for cleaning purposes, the effects of the emissions are included in the exergy analyses as the minimum exergy consumption necessary to achieve zero environmental impact [31]. The exergy of the different gases calculated before can be viewed as the minimum exergy required for recovering these gases from the environment. The direct carbon dioxide and carbon monoxide emissions from primary aluminum reduction process associated with the different technologies have been estimated previously (Table 6). The CO₂ emission that results from electricity generation and material processing is considered below.

5.3.1. CO₂ Emission from Electricity Generation

Table 13 shows the emission factor of carbon dioxide that results from different fuel sources during electricity generation in the US [39]. The fraction of electricity generation for each source is also given in the same table [40].

Table 13. Average CO₂ emission factor and fraction of electricity generation for each source in the US and primary aluminum industry.

Source	CO ₂ Emission (kg/kg of Fuel)	CO ₂ Emission (kg/MJ of Fuel)	CO ₂ Emission (kg/MJ of Electricity) ^a	U.S. Average (%)	Primary Aluminum Industry ^b (%)
Coal	2.14	0.063	0.19	53.7	30.1
Natural Gas	1.98	0.038	0.12	9.6	5.4
Fuel Oil	3.52	0.075	0.23	4	2.25
Nuclear	0	0	0	21.9	12.3
Hydroelectric	0	0	0	10.8	50

^a Assuming 33% conversion efficiency; ^b the values are calculated assuming 50% of electricity is produced by the hydroelectric source and the remaining 50% is distributed among the other sources according to their contributions to the entire US.

The weighted average CO₂ emission for the US and smelting process can be estimated as follows:

$$\begin{aligned}
 \text{CO}_2(\text{U.S.}) &= 0.19 \times 0.537 + 0.12 \times 0.096 + 0.23 \times 0.04 + \\
 &0 \times 0.219 + 0 \times 0.108 = 0.123 \text{ kg/MJ of electricity} = 0.444 \text{ kg/kWh of electricity} \\
 \text{CO}_2(\text{smelting}) &= 0.19 \times 0.301 + 0.12 \times 0.054 + 0.23 \times 0.0225 + \\
 &0 \times 0.123 + 0 \times 0.5 = 0.069 \text{ kg/MJ of electricity} = 0.249 \text{ kg/kWh of electricity}
 \end{aligned}
 \tag{22}$$

5.3.2. CO₂ Emission from Alumina and Carbon Anode Productions

Using the quantity of energy used in alumina and carbon anode production from Tables 11 and 12, respectively, and the emission factor of carbon dioxide from Table 13, the carbon dioxide emissions from alumina and anode production are presented below.

For alumina,

$$\begin{aligned} \text{CO}_2 &= 0.093 \text{ kg of oil} \times 3.52 \frac{\text{kg of CO}_2}{\text{kg of oil}} + \\ &0.17 \text{ kg of natural gas} \times 1.98 \frac{\text{kg of CO}_2}{\text{kg of natural gas}} + \\ &0.109 \text{ kWh} \times 0.444 \frac{\text{kg of CO}_2}{\text{kWh}} = 0.712 \frac{\text{kg of CO}_2}{\text{kg of alumina}} \end{aligned} \quad (23)$$

For carbon anode (assuming zero carbon dioxide emissions associated with the production of petroleum coke, pitch, and green coke),

$$\begin{aligned} \text{CO}_2 &= 0.004 \text{ kg of oil} \times 3.52 \frac{\text{kg of CO}_2}{\text{kg of oil}} + \\ &0.073 \text{ kg of natural gas} \times 1.98 \frac{\text{kg of CO}_2}{\text{kg of natural gas}} + \\ &0.266 \text{ kWh} \times 0.249 \frac{\text{kg of CO}_2}{\text{kWh}} = 0.225 \frac{\text{kg of CO}_2}{\text{kg of carbon anode}} \end{aligned} \quad (24)$$

5.4. Final Model Summary

The direct energy, material, and environmental impact of primary aluminum production using different technologies is shown in Table 6. These direct values can now be converted into their respective source exergies. The summation of the source exergies of the energy, material, and environmental impact is termed equivalent exergy. The final results are shown in Table 14 and Figure 9.

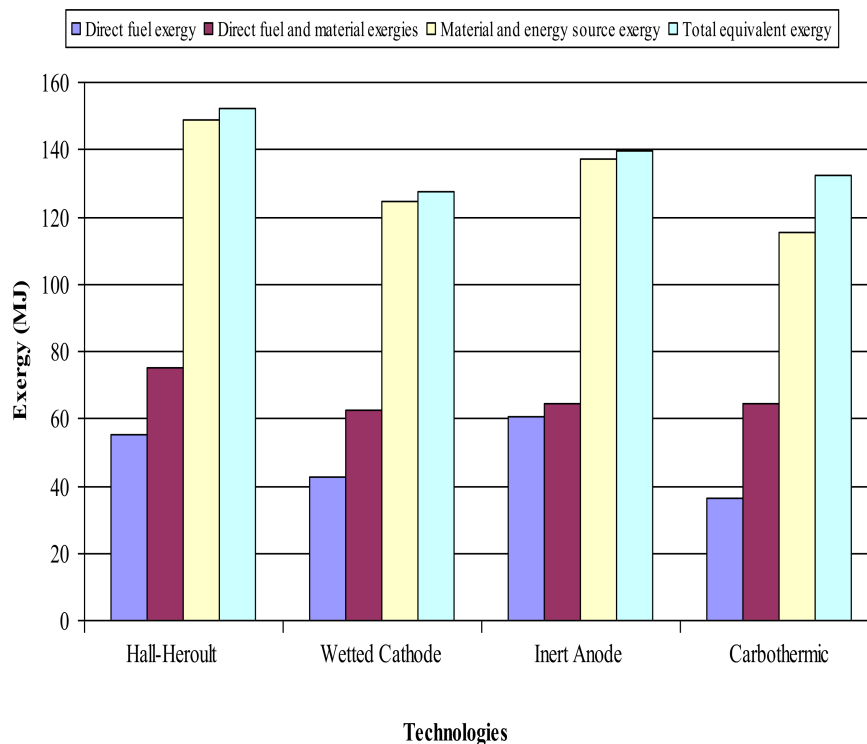


Figure 9. Comparison of different primary aluminum technologies.

Table 14. Results summary for the different technologies (per 1 kg of Al).

Technology Name		Hall-Heroult	Wetted Cathode	Inert Anode	Carbothermic
Direct fuel exergy requirement (MJ)		55.33	42.59	60.55	36.54
Source fuel exergy requirement (MJ)		104.89	80.73	114.78	69.26
Direct material exergy requirement (MJ)	Anode	16.11	16.11	0	0
	Alumina	3.83	3.83	3.83	3.75
	Carbon	0	0	0	23.99
Resource material exergy requirement (MJ)	Anode	21.53	21.53	0	0
	Alumina	22.5	22.5	22.5	22.04
	Carbon	0	0	0	23.99
Environmental Impact (kg)	CO ₂	6.96	6.08	5.56	3.87
	CO	0	0	0	1.56
Environmental Impact(MJ)	CO ₂	3.13	2.74	2.50	1.74
	CO	0.00	0.00	0.00	15.33
Total direct fuel exergy (MJ)		55.33	42.59	60.55	36.54
Total direct fuel and material exergy (MJ)		75.27	62.53	64.38	64.28
Total source exergy (MJ)		148.92	124.76	137.28	115.29
Total exergy equivalent (MJ)		152.05	127.50	139.78	132.36

(1) Total direct fuel exergy includes only the exergy content of the electricity input to the process; (2) This also includes the exergy content of the material input to the process in addition to (1); (3) This includes the source exergy of the electricity and material inputs to the process; (4) This includes the environmental impact in addition to (3).

According to the traditional energy analysis that tries to minimize the energy input, carbothermic technology will be the first choice, followed by the wetted drained cathode, the Hall–Heroult method, and finally, inert anode technology. When also considering the direct input of the materials, the wetted drained cathode technology becomes the best available choice, followed by the carbothermic, the inert anode, and finally, the Hall–Heroult technology. If we consider the exergy consumed during energy and material processing, the carbothermic technology will be the first choice, followed by the wetted drained cathode, the inert anode, and finally, the Hall–Heroult technology. By considering the source exergy of the energy, material, and the environmental impact, the wetted cathode technology offers the lowest exergy consumption, followed by the carbothermic, the inert anode, and finally, the Hall–Heroult technology.

6. Conclusions

In the current Hall–Heroult aluminum production process, there is significant opportunity to further reduce energy requirements and environmental impact. The recent interest in environmental change clearly implies that energy and environmental policies should be more closely interrelated. For this reason, this paper examined and compared the different primary aluminum technologies using the equivalent exergy concept as a decision tool. This concept makes the analysis more complete by taking into consideration the direct exergy contents of the fuel and materials, their production exergies, and the exergy required to clean the emissions. The application of this concept to the different primary aluminum production technologies emphasizes that, in order to optimize the process, it is necessary to consider the exergies of energy, material, the environmental impact, and their associated exergy production. The results show that the wetted drained cathode technology offers the lowest exergy consumption, followed by the carbothermic, the inert anode, and finally, the Hall–Heroult. If the wetted drained cathode technology is adopted, it will result in 16.15% exergy savings compared with the current Hall–Heroult technology.

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Conflicts of Interest: The authors declare no conflict of interest.

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