Ola Hunstad Ask

Life Cycle Assessment of Primary Aluminium Production by Hydrogen Diffusion Anode

Master's thesis in Industrial Ecology
Supervisor: Johan Berg Pettersen
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The following is the original problem description, which has been altered during the course of this study due to increased knowledge and understanding.

Aluminium is strong, lightweight and highly resistant to corrosion, and is widely used in building construction, aircraft construction, consumer electronics and power lines. Primary aluminium production is responsible for around 3% of the world's industrial CO2 emissions, where the calcination of alumina accounts for most of the emissions. The electrolysis process of aluminium is highly electricity consuming, and while most producers are using renewable energy sources, an alternative process could reduce the use of electricity. Hence, the pressure on the electrical grid could be reduced, enabling the transition to renewable power sources.

Hydrogen is one of the most promising alternative fuels, where the emission from combustion is water only. Hydrogen produced from green energy sources or from aluminium scrap will greatly reduce the environmental impact of aluminium production.

Empirical data for current aluminium production is well documented by the producers, but the use of hydrogen in aluminium production is still at the research stage, with very little empirical data available. Hydrogen is not implemented in any production process, but the environmental benefits could be significant, so that research into how and where in the production process hydrogen has possible uses needs has large potential.

This thesis will investigate the effect of introducing hydrogen in the production process:

- What effect will the use of hydrogen in the calcination process of alumina have on various environmental impact categories?
- Can hydrogen be reacted with alumina to replace the traditional Hall-Heroult process, to make the process less electricity demanding?
- Is producing hydrogen from reacting aluminium dross/scrap with water in the production facility a viable option to enhance circularity and hence reduced emissions?

This thesis aims at producing a system description and a model for process simulation, which will be used to perform a Life Cycle Assessment (LCA) of primary aluminium production process. An existing simulation model for primary aluminium production will be expanded to incorporate the use of hydrogen in the production process.

The process simulation software HSC Chemistry will be used for modelling the process, and the life cycle assessment software SimaPro will be used to perform the LCA of the process/system.

Abstract

Aluminium is an important metal for the transition to net zero emission, widely used in renewable power generation construction and as a construction material for buildings. The conventional production method emits 1.5 kg CO_2 per kg aluminium due to the consumption of the carbon anode. In this master's thesis, an alternative approach is investigated, by substituting the prebaked carbon anode with a hydrogen diffusion anode. The proposed production route could reduce the GHG emission from the electrolysis significantly, and a Life Cycle Assessment (LCA) is developed to compare the environmental performance of the conventional carbon anode route and the alternative hydrogen diffusion anode production route.

To identify hotspots of the production routes, four sensitivity analyses were carried out, investigating the robustness to change in electricity source, fuel source and production methods for hydrogen fluoride and hydrogen.

The results show that the direct effect of changing to hydrogen diffusion anode is a significant reduction in GHG emissions and a moderate reduction in the remaining categories. When including the hydrogen fluoride waste emission as a by-product, the impacts experienced a significant reduction in almost every category. The energy source for the many heat and electricity-demanding processes highly affects the environmental performance of the production routes.

Hydrogen diffusion anode reduces environmental impacts, while recycling of hydrogen fluoride results in a further reduction.

Sammendrag

Aluminium er et viktig metall for overgangen til netto nullutslipp, mye brukt i fornybar kraftproduksjonskonstruksjon og som konstruksjonsmateriale for bygninger. Den konvensjonelle produksjonsmetoden slipper ut 1.5 kg CO_2 per kg aluminium på grunn av forbruket av karbon ved anoden. I denne masteroppgaven undersøkes en alternativ tilnærming, ved å erstatte karbonet med en hydrogendiffusjonsanode. Den foreslåtte produksjonsruten kan redusere klimagassutslippene fra elektrolysen betydelig, og en livssyklusanalyse (LCA) er utviklet for å sammenligne miljøytelsen til den konvensjonelle produksjonsmetoden og den alternative produksjonsmetoden med hydrogenanode.

Fire sensitivitetsanalyser ble utført for å identifisere viktige prosesser i produksjonen, og undersøkte robustheten overfor endringer i energikilde for elektrisitet og varme og produksjonsmetoder for hydrogenfluorid og hydrogen.

Resultatene viser at den direkte effekten av å bytte til hydrogenanode er en betydelig reduksjon i klimagassutslipp og en moderat reduksjon i de resterende kategoriene. Når man inkluderer utslipp av hydrogenfluoridavfall som et verdifullt biprodukt, var resultatet en betydelig reduksjon i nesten alle kategorier. Energikilden til de mange varme- og elektrisitetskrevende prosessene påvirker i stor grad miljøpåvirkningen til de to alternativene.

Hydrogendiffusjonsanode reduserer miljøpåvirkningen mens resirkulering av hydrogenfluorid gir en ytterligere reduksjon.

Acknowledgements

Contents

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List of abbreviations and symbols

Al	Aluminium
Al^{3+}	Aluminium ion
AlF$_3$	Aluminium fluoride
ALFED	Aluminium Federation
Al$_2$O$_3$	Aluminium oxide (alumina)
ALCA	Attributional LCA
AoP	Areas of Protection
APOS	Allocation at Point of Substitution
C	Carbon
C$_2$F$_6$	Hexafluoroethane
CaF$_2$	Calcium fluoride (fluorspar)
CF$_4$	Tetrafluoromethane
CH$_4$	Methane
CLCA	Consequential LCA
CO	Carbon monoxide
CO$_2$	Carbon dioxide
Cu	Copper
DCB	Dichlorobenzene
DALY	Disability-adjusted life years
EA	European Aluminium
Eq.	Equivalent
F.U.	Functional Unit
GHG	Greenhouse gas emission
GLO	Global (in ecoinvent)
GWP	Global Warming Potential
(H/A)	Hierarchist approach / average weighting
H$^+$	Hydron
H$_2$	Hydrogen
H$_2$O	Water
H$_2$SO$_4$	Sulphuric acid
HF	Hydrogen fluoride
HSC	HSC Chemistry 10 Software
IAI	International Aluminium Institute
IEA	International Energy Agency
IRP	Ionising Radiation Potential
ISO	International Organization for Standardization

LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
Na	Sodium
Na$_2$O	Sodium oxide
Na$_2$CO$_3$	Sodium carbonate
Na$_3$AlF$_6$	Cryolite
NaAlF$_4$	Sodium aluminium tetrafluoride
N	Nitrogen
NO	Norway (ecoinvent)
NH$_3$	Ammonia
VOCs	Volatile Organic Compounds
NO$_x$	Nitrogen oxides
OH$^-$	Hydroxide
O$_2$	Oxygen
P	Phosphorus
Pt	Weighted points
RER	Europe (in ecoinvent)
RoW	Rest-of-the-World (in ecoinvent)
SGA	Smelter Grade Alumina
SO$_2$	Sulphur dioxide
SOP	Surplus Ore Potential
TP	Toxicity Potential
TAP	Terrestrial Acidification Potential
U	Unit (in ecoinvent)
UV	Ultra violet (radiation)

Chapter 1

Introduction

1.1 Background

The most recently published annual report from the Intergovernmental Panel on Climate Change (IPCC) stated that the increase in carbon dioxide and methane concentration in the atmosphere (47 % and 156 %, respectively) over the last 250 years has far exceeded the natural variations over the last 800 000 years [1]. In addition, the global surface temperature has increased more in the last 50 years (around 1 °C) than in any fifty-year period in the last 2000 years [1]. As a response to this, 191 countries are currently Parties to the Paris Agreement, an international UN treaty aiming at reaching net-zero carbon emissions by 2050 and to limit the global temperature rise to 1.5 °C above pre-industrial levels [2].

To reach these goals, the green house gas (GHG) emissions must be reduced significantly by increasing renewable power generation, decarbonising the global energy sector, industrial processes and transport industry by developing new technology and more electronic system control [3]. More renewable energy sources are needed, more power transmission systems are needed, more electronic components are needed, and energy usage must be more thoroughly monitored and controlled. In this transition to a more sustainable and technology-oriented future, aluminium is a significant contributor.

Aluminium is lightweight, strong, highly malleable, corrosion-resistant and infinitely recyclable. Due to its ductility, heat conductivity and reflectivity characteristics, it is the most used material in solar power applications [4]. It has high electric and heat conductivity-to-weight ratio, making it highly suitable for power transmission lines, heat exchangers, heat sink in batteries and many other electrical products [5]. Aluminium is used in wind turbines, aeroplanes and other constructions exposed to the weather due to its high durability caused by the non-corrosive properties [4]. It can aid in decarbonising the mobility and transportation industry by reducing energy demand and hence emissions, using aluminium in a range of components makes the vehicles lighter [5].

The global demand for aluminium was 95 million tonnes (Mt) in 2018, where two-thirds were met by primary aluminium, and this demand is forecast by the International Aluminium Institute (IAI) [6] to increase by up to 80 % by 2050. Despite the increased focus on recycling, the demand for primary aluminium might be as high as 90 Mt within the next 25 years [6]. To reach the common goal of net zero emission by 2050 by EA, IAI and Aluminium Federation (ALFED) [6–8], the industry must decarbonise the production process at a rapid pace and increase recycling [6, 8].

Today's primary aluminium production process used in all industrial primary aluminium production is the Hall-Héroult process [9]. It is an electrochemical process by which solid aluminium oxide is dissolved in molten cryolite and electrolytically reduced with carbon to produce liquid aluminium and gaseous carbon dioxide [10].

This is the most economically viable production method, but it is a highly energy-intensive process, requiring large amounts of electric power for the electrolysis, with a world average of 14.1 MWh per tonne liquid aluminium [11]. Globally, 67 % of this electricity is produced by fossil energy sources [12], giving rise to indirect GHG emissions of just above 10 t CO_2 per t liquid aluminium [13]. The second main contributor to GHG emissions is the direct emissions from consumption of the carbon anode, which amounts to 1.5 tonne CO_2 per tonne liquid aluminium [14].

To reach the 1.5 degrees goal of The Paris Agreement [2], the aluminium sector must reduce the CO_2 emissions to 53 Mt CO_2-eq. in 2050 [15]. The challenges regarding energy consumption in the smelting cell are difficult to overcome in the Hall-Héroult process, which is close to the limit of possible current efficiencies [10]. This means that industrial aluminium smelters today must aspire to decarbonise their power supply as a short-term contribution, to reduce the indirect emissions for the production process. At the same time, it is important to develop further and optimise the process, and research possible methods to improve the existing process within the existing production facilities and infrastructure. Changing from today's Hall-Héroult process to a brand new process is a large and expensive exercise, so finding parameters of the existing process that can be decarbonised is highly important.

This study will investigate one of the areas of improvement, the direct CO_2 emissions from the use of consumable carbon anode. The effect of replacing the carbon anode with a hydrogen diffusion anode will be studied. The conventional production of primary aluminium is explained in Chapter 1.2, while the hydrogen anode option will be explored in Chapter 1.3. Life Cycle Assessment (LCA) is used to interpret the environmental impacts, sustainability and the difference between the conventional production route and the hydrogen anode production route. The main goal and research questions are defined in Chapter 3.2.

1.2   Primary aluminium production route

As mentioned in Chapter 1.1, aluminium is widely used in energy and technology applications needed for the decarbonising, necessary to slow global warming. Historically,

metallic aluminium was first identified in 1808, when the English chemist Sir Humphry Davy identified a metal base of alumina which he termed alumina/aluminium. In 1825 a Danish chemist produced the first impure metal form of alumina, and in 1886 the American chemist Charles Martin Hall and the French chemist Paul Héroult, independently patented the electrolytic process. At the same time two different inventions were made that significantly impacted the production of metallic aluminium, namely the dynamo by W. Siemens in 1867 to produce electricity and the Bayer process by K. Bayer in 1887 [9].

The electrolytic process from 1886 is called the Hall-Héroult process and is the process exclusively used in industrial aluminium production globally today [16]. It is an electrochemical process where solid aluminium oxide (Al_2O_3) is dissolved in molten cryolite (Na_3AlF_6) and electrolytically reduced with carbon (C) to produce liquid aluminium (Al) and gaseous carbon dioxide CO_2 [10]. The overall production process of primary aluminium is shown in Figure 1.1 [17]. The left part of the figure, ending at liquid aluminium, shows the reduction cell which will be the focus of this study.
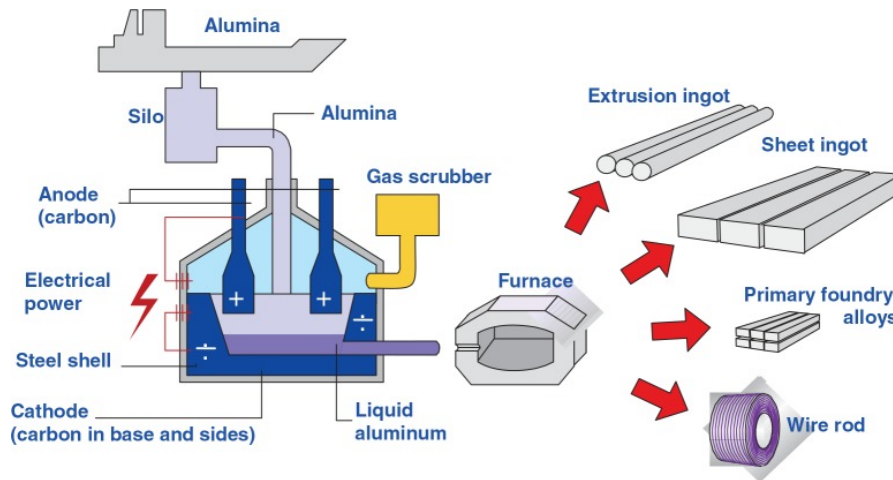
Figure 1.1: Flow chart of the primary aluminium production process, from aluminium oxide to ingots, from Kvande et. al [17].

Solid alumina is fed to the cell and dissolves in the electrolyte. Electricity is distributed through the cell from the positively charged anode to the negatively charged cathode. The Al_2O_3 is reduced by the carbon at the cathode, while liquid aluminium and CO_2 are produced at the anode. The overall chemical reaction occurring is represented by Equation (1.1) [10].

$$\frac{1}{2}\,Al_2O_3\,(diss) + \frac{3}{4}\,C\,(s) \rightleftharpoons Al\,(l) + \frac{3}{4}\,CO_2\,(g) \tag{1.1}$$
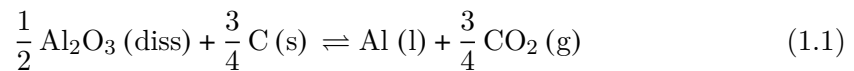
The reduction cell is made of a steel shell lined with refractory materials for thermal insulation, and on the inside the steel is lined with graphite to contain the corrosive molten cryolite and the molten aluminium [10]. The carbon bottom lining is called the

cathode, but the liquid aluminium accumulating on the cathode surface has very high electrical conductivity and acts in reality as the cathode [14]. The liquid aluminium is tapped from the bottom of the cell [16], then cast into ingots or foundry alloys [9]. This thesis will not consider the steps after the liquid aluminium.

The electrolysis process is a simple but at the same time complex process. There are several different side and intermediate reactions, complete and partially reacted, that describe what happens in the bath during electrolysis. This chapter describes the most important reactions relevant to the scope of this study, while Appendix A provides a more comprehensive overview of the chemical reaction equations for the process.

The reduction of alumina, in Equation (1.1), has a decomposition voltage (E^0) of -1.19 V, meaning it is a non-spontaneous chemical reaction, and the reaction needs either an applied voltage of at least 1.19 V or thermal energy of 606 kJ/mol Al (6.24 kWh/kg Al)) to proceed [16, 18]. Driving a non-spontaneous reaction using electricity as the driving force to decompose the metal oxide into a metal is called electrolysis [19]. Electricity is the flow of ions or electrons, and to enable the separation of the aluminium and oxygen compounds, the ions in the aluminium oxide must be free to move [14]. This can be achieved by melting the solid Al_2O_3, but the high melting point of 2 000 °C [20] makes it challenging to perform electrolysis on pure molten alumina due to material and process challenges [9]. The alternative is to dissolve the Al_2O_3 in a suitable electrolyte [10]. The electrolyte has four main functions, to act as a solvent for Al_2O_3, to provide electrical conductivity from the anode to the cathode, to provide a physical separation between the liquid aluminium at the cathode and the CO_2 gas at the anode, and to act as an ohmic resistor in the cell, producing heat from the electricity to make the cell self-heating [17].

Aluminium oxide has a hexagonal crystal lattice, which creates strong chemical bonds with the oxygen atoms. In an aqueous solution the high reactivity with the protons of the water results in a reduction of H^+ instead of Al^{3+} ions. In other words Al_2O_3 insoluble in water because the water cannot react with the oxide ions, and an electrolyte with high solubility of Al_2O_3 must be used, a molten aluminium salt electrolyte made of cryolite (Na_3AlF_6) [16]. The cryolite has a lower melting point than Al_2O_3 at 1 011 °C [21] and high ionic conductivity [19, 22], allowing the ions to move freely at lower temperatures [18]. In addition, the viscosity of Na_3AlF_6 is lower than that of liquid aluminium [21, 23], which makes the liquid aluminium accumulate at the bottom of the cell, making the tapping process easier [10].

The Na_3AlF_6 is composed of sodium fluoride (NaF) and aluminium fluoride (AlF_3), and the NaF/AlF_3 ratio is called the cryolite ratio[24]. It is 3 for pure cryolite, but excess AlF_3 is added to obtain an even lower melting point, resulting in an industrial cryolite ratio of 2-3 and a melting point of 945-955 °C [9, 17]. The electrolytic reduction process is a mix of batch operations and continuous electrolysis. The batch operations of anode change, aluminium oxide feeding and tapping impose slight changes to the temperature in the cell [14]. That is why reduction cells are typically operated at temperatures around 10 °C higher than the melding point, and this difference is called the superheat [25]. This provides operational stability in the cell, since changes in temperature affect

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the thickness of the frozen side ledge, and hence the heat balance of the cell. This solidified cryolite (frozen crust), is used to provide thermal insulation and protect the carbon lining from the corrosive bath [26]. The typical bath composition is 12 wt % of AlF_3, 5 wt % of CaF_2 and 3 wt % of Al_2O_3 [9, 27], and the typical operational temperature is 960 °C [9].

By lowering the melting point, the cell can be operated at a lower temperature, which at the same time reduces the Al_2O_3 solubility in the bath [28]. This requires good control on Al_2O_3 feeding, and most modern smelter cells use point-feeders to add 1-2 kg every other minute [17]. If the Al_2O_3 concentration in the bath becomes too low, the cell experience an anode effect, a situation where the cell voltage increases from 4-4.5 V to 20-50 V in a short time [14]. During this state two gases with very high global warming potential are produced, tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6), which require manual intervention to stop [29].

The total stoichiometric reaction enthalpy (ΔH^0_{tot}) is 606 kJ/mol, or 6.242 kWh/kg Al [16, 18, 30], but smelter cells typically operate at twice this value [9]. To form the aforementioned frozen electrolyte side ledges the heat flux through the walls must be very high, to cool the electrolyte enough to freeze at the wall [16]. This results in significant heat loss through the walls and high energy consumption [24]. The specific electric energy consumption of a reduction cell can be calculated from Equation (1.2) [16, 18].

$$W_{el} = EC = \frac{E_{cell}\,F\,v_e}{3600\,M_{Al}\,CE\,v_{Al}} = 2.98 \cdot \frac{E_{cell}}{CE} \tag{1.2}$$

Over 90 % of Al_2O_3 used in modern cells consists of γ-Al_2O_3 [9], which converts to the α-Al_2O_3 which is in equilibrium with the electrolyte at the operational cell temperature of 960 °C [10].

The main impurities of the Al_2O_3 are Na_2O and CaO, which are neutralised by aluminium fluoride (AlF_3) in the bath to form Na_3AlF_6 and CaF_2, according to the reactions in Equation (1.3) and (1.4) respectively [28].

$$3\,Na_2O + 4\,AlF_3 = 2\,Na_3AlF_6 + Al_2O_3 \tag{1.3}$$

$$3\,CaO + 2\,AlF_3 = 3\,CaF_2 + Al_2O_3 \tag{1.4}$$
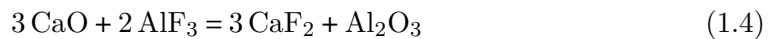
The basic function of the cathode is to act as an electric conductor and to contain the molten aluminium [25]. The aluminium ions (Al^{3+} cations) of Al_2O_3 are reduced to liquid aluminium at the electrolyte-metal interface of the cathode, and the half-reaction is described in Equation (1.5) on the next page [16, 19].

$$Al^{3+}\,(bath) + 3\,e^- = Al\,(l) \tag{1.5}$$

The basic function of the anode is to act as an efficient converter of chemical energy, and the surface of the carbon anode is consumed by the release of energy in the presence of oxygen [10]. Oxide ions (anions) from the dissolution of Al_2O_3 are electrolytically discharged onto the anodes as an intermediate product as of Equation (1.6), and then oxidised by the carbon of the anode, gradually consuming the anode by the formation of gaseous CO_2 [9] as of Equation (1.7) [16, 19].

$$2\,O_2 = O_2 + 4\,e^- \tag{1.6}$$

$$\frac{3}{2}\,O^{2-} + \frac{3}{4}\,C = CO_2\,(g) + 3\,e^- \tag{1.7}$$
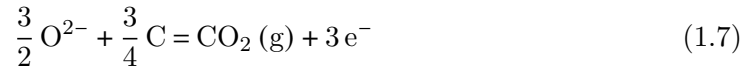
One of the main issues with the conventional primary aluminium production process is the consumption of carbon [16]. The main reaction from Equation (1.1) earlier in this chapter consumes carbon and produces CO_2. A similar reaction is possible, with CO as a product instead of CO_2, but studies have shown that oxidation of CO to produce CO_2 is shifted far towards CO_2 [31], and hence the overall reaction producing CO_2 is the most likely. Carbon is consumed at a higher rate than the theoretical for this reaction, mostly by the re-oxidation of Al [10, 31] and the reaction between CO_2 and solid carbon particles in the bath [31, 32], represented by Equations (1.8) and (1.9).

$$Al\,(l) + \frac{3}{2}\,CO_2\,(g) \rightarrow \frac{1}{2}\,Al_2O_3\,(diss) + \frac{3}{2}\,CO\,(g) \tag{1.8}$$

$$CO_2\,(g) + C\,(s) = 2\,CO\,(g) \tag{1.9}$$
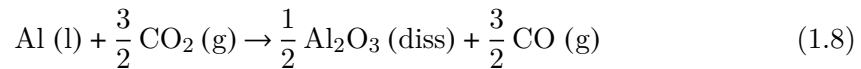
The anodically CO_2 emissions could be eliminated by using an inert anode. The cathode reaction for an inert anode is the same as for a carbon anode from Equation (1.5), while the anode reaction differs and is described by Equation (1.10) [16, 33].

$$\frac{1}{2}\,Al_2O_3\,(s) = Al\,(l) + \frac{3}{4}\,O_2 \tag{1.10}$$
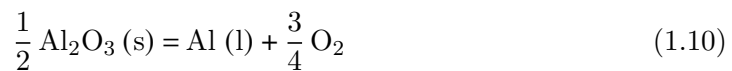
The decomposition voltage of the inert reaction is 2.2 V at 960 °C, about 1 V higher than the carbon anode [34]. This could be reduced by minimising the ohmic voltage drop in the electrolyte, requiring a highly redesigned cell [34].

No material for inert anode has proved to withstand the highly corrosive environment [33], and one possible solution to these issues is to use a reducing gas, where CH_4 and hydrogen are proposed [35–37]. This option will be further explained in the next chapter.

A presentation of the chemical reactions in the electrolysis cell not shown in this chapter is found in Appendix A.

1.3   Hydrogen diffusion anode

As explained in Section 1.2 the basic principles of the production process are mostly unchanged since it was proposed, but there have been significant technological improvements over the years. Key performance indicators like current efficiency, energy consumption and cell size are close to the best performance practically possible [9], but the direct GHG emissions from the carbon anode have the potential of reducing the environmental impacts of the primary aluminium production.

Braaten et. al [38] investigated a non-electrolytic path, where hydrogen was dissolved in molten aluminium. The paper showed that aluminium might possibly be formed at 1 200 °C, but the conclusion where that the temperature must be above 2 000 °C for the reaction to occur at a reasonable rate[1].

One of the possible solutions is to use a gas anode, where hydrogen (H_2) as a reducing gas is supplied to the anode [34]. The goal of introducing a reducing gas is to depolarise the anode, resulting in lower anode potential and reduced cell voltage and energy consumption [33]. The reduction of Al_2O_3 with hydrogen as a reducing gas supplied to the anode, producing liquid aluminium and steam is shown in Equation (1.11) below [37].

$$\frac{1}{2}\,Al_2O_3\,(s) + \frac{3}{2}\,H_2\,(g) \rightleftharpoons Al\,(l) + \frac{3}{2}\,H_2O\,(g) \qquad (1.11)$$
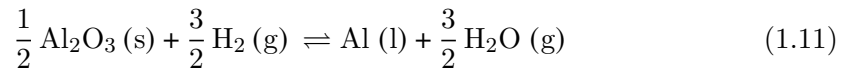
This reaction has a decomposition potential of 1.28 V at 960 °C, similar to the conventional anode process and 1 V lower than the inert anode [37]. The theoretical amount of H_2 to produce 1 tonne of molten aluminium is 0.11 t, resulting in 1 t H_2O in the off-gas. At the anode, the hydrogen can react in multiple different ways, but the main reaction is the one described in Equation (1.12) below [37].

$$H_2 = 2\,H^+ + 2\,e^- \qquad (1.12)$$

The introduction of hydrogen to the cell at the expense of carbon effectively eliminates the anodic CO_2 emissions from the carbon consumption of the anode, as seen from the overall reactions in Equation (1.1) and (1.11) [34]. The overall reaction of Al_2O_3 and H_2 theoretically produce only H_2O vapour as a by-product [14], but as mentioned in Section 1.2, the process is comprehensive and complex and results in waste emissions other than that of the main reaction [10, 39].

The main concern when introducing hydrogen to the cell is the increased generation of one of these emissions, the hydrogen fluoride (HF) emissions, as the hydrogen content in the cell increases [37]. The emissions are promoted by hydrogen content in the cell, introduced to the cell by moisture from alumina, ambient air moisture and residual hydrogen content of the anode [40].

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[1]Halvor Kvande, PhD and Doctor Technicae, retired at NTNU (personal communication, November 19, 2021)

HF is a colourless, toxic, highly corrosive, non-flammable chemical compound in the form of a gas or fuming liquid [41]. It is highly water-soluble, and the aqueous solution of HF is called hydrofluoric acid [42]. Fluorides as fluoride ions are naturally in many rocks, minerals and soils as fluoride ions, and are the 13th most abundant element, comprising around 0.06 % of the Earth's crust [41]. These fluorides are released through weathering and dissolution of minerals, and through emissions from volcanoes and marine aerosols [43]. The gas is highly soluble in water, and dissolves in clouds, fog and rain, impacting the environment as acid rain, contaminating the groundwater [43].

In industrial settings, nearly 60 % of the HF is used to produce refrigerants, the other major uses being as a catalyst in petroleum refining (to produce high-octane gasoline), to make uranium hexafluoride (UF_6 needed to separate uranium isotopes in nuclear power plants) [44] and in the semiconductor industry [42]. In the semiconductor production process it is used in the native oxide etching of silicon wafers [45]. The corrosive quality of HF makes it a valuable ingredient in rust and stain removers [46].

In adequate amounts, fluoride helps bone mineralisation and dental enamel formation in humans [43], while exposure to higher concentrations affects the metabolic processes [47]. Exposure to gaseous HF causes irritation to the eyes and respiratory system, and could result in lung diseases, e.g., fluid accumulation in the lungs (pulmonary oedema) [41]. Direct contact with aqueous HF can cause severe burns which can damage internal tissue since the HF easily penetrates skin and tissue and causes poisoning, skin ulcers and blindness if contact with the eyes [42]. Chronic exposure can lead to skeletal fluorosis which causes increased bone density, joint pain and restricted joint movement [47] or chronic lung diseases [43].

The conventional production process of hydrogen fluoride is the reaction between fluorspar and sulphuric acid (H_2SO_4) [48]. The fluorite ore is mined and purified to acid grade fluorspar (98 % CaF_2), as of the reaction in Equation (1.13) below [48].

$$CaF_2 + H_2SO_4 = 2\,HF + CaSO \tag{1.13}$$

They are mixed with fluorspar to a slurry and heated to around 900 °C in rotary kilns for several hours [48]. The solid waste and sulphuric acid are removed, while the hydrogen fluoride gas is collected and purified through distillation in copper or steel vessels, and either condensed and stored as liquefied gas or diluted with water to obtain hydrofluoric acid [49]. This production process is the most widely used industrial method globally, and the burning of natural gas provides heat. China accounts for over 50 % of the global production of hydrogen fluoride, with Germany the second largest manufacturer [50].

The HF gas is generated in the cell through hydrolysis of a hydrogen source with a reactive fluoride in either liquid or gaseous phase [51]. In the liquid phase an electrochemical hydrolysis of the bath occurs, while thermal hydrolysis of the pot gas occurs in the gaseous phase [52]. HF evolution/emissions can be characterised as gaseous or particulate fluorides, where gaseous fluorides are those which continue to be in the gas phase at ambient temperature, mainly HF, CF_4 and C_2F_6 [40]. Particulate or volatilised bath are the fluorides which become particulate at ambient temperature [40].

The main sources of hydrogen are ambient air moisture, moisture in primary alumina and residual hydrogen content in the anode, while the major fluoride species reacting with the hydrogen sources are AlF_3, $NaAlF_4$ and Na_3AlF_6 [40, 52, 53]. The mechanisms and different hydrogen sources are schematically presented in Figure 1.2, and will be further explained during the course of this chapter.
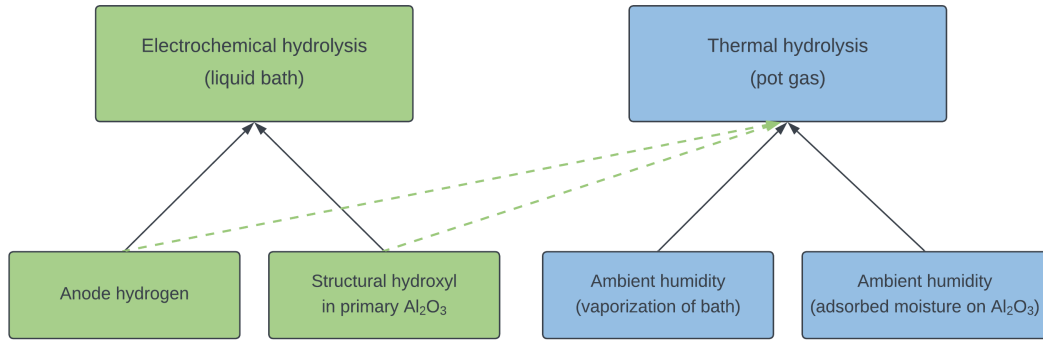
Figure 1.2: Schematic view of the contribution to HF generation from the different hydrogen sources in a cell, from Hyland et al. [52]

As illustrated in Figure 1.2 the electrochemical hydrolysis of the liquid bath involves the structural water in alumina (OH^-) and the anode hydrogen content, while the thermal hydrolysis of pot gas involves ambient humidity as adsorbed moisture on the alumina or direct air humidity and small amounts of unreacted hydrogen from the anode and the Al_2O_3 [54].

Hyland et al. [52] studied the HF levels in the duct gas and found that smelter grade alumina (SGA) represented the largest single contributor to HF evolution, as illustrated in Figure 1.3 on the next page.
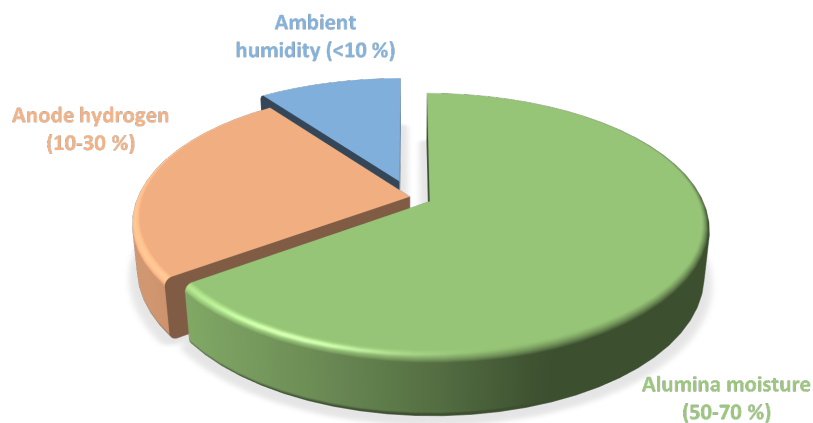
Figure 1.3: Schematic view of the relative contribution to HF generation from the three major hydrogen sources in a cell, from Hyland et al. [52]

The electrochemical hydrolysis occurs inside the electrolyte and is called primary generation of HF, while the thermal hydrolysis occurs in the duct gas under and is called secondary generation of HF [53].

Hydrolysis of bath

The electrochemical hydrolysis of the liquid bath, also called dissolved water hydrolysis, occurs when the structural water in the Al_2O_3 and the hydrogen content of the anode react with the liquid bath, either directly with Na_3alF_6 or with fluorides in the form of AlF_3 or $NaAlF_4$ [40].

The hydrogen content of prebaked anodes is thermodynamically stable, but since the anode potential is relatively high (around 1.5 V), multiple oxidation reactions are possible [53]. The two main reactions are hydrogen reacting with the Na_3AlF_6 or the dissolved AlF_3 to produce HF as of Equation (1.14) [37, 53, 55] and (1.15) [33, 56].

$$2\,Na_3AlF_6\,(l) + 3\,H_2\,(g) = 2\,Al\,(l) + 6\,NaF\,(l) + 6\,HF\,(g) \tag{1.14}$$

$$2\,AlF_3\,(diss) + 3\,H_2\,(g) = 2\,Al\,(l) + 6\,HF\,(g) \tag{1.15}$$
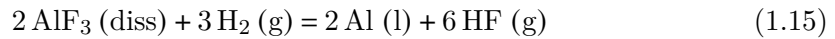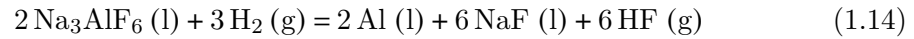
Patterson et al. [53] concluded with an average hydrogen conversion factor of 10 %, consistent with the 8 % value by Wahnsiedler et al. [51] (also used by Haupin and Kvande [40]). Hydrogen anode content contributes to around 8 % of the total HF emissions [53]. "The remainder of the unreacted hydrogen either forms part of the dissolved water content in the bath or is transported to the extraction system via the crust vents where it could aid in secondary HF generation" [53].

Dissolved water in primary alumina and adsorbed moisture on the anode during anode change introduces moisture to the cell [53]. The Al_2O_3 used in modern cells has a structural hydroxyl (OH^-) content which results in a dissolved H_2O concentration in the bath [52], and is the major contributor to HF generation during the electrolysis [53]. The main fluoride specie reacting with the structural water is believed to be AlF_3 because of its significantly higher equilibrium coefficient compared to other fluoride species [14, 40]. The hydrolysis reaction between the dissolved H_2O and AlF_3 is represented by Equation (1.16) [29, 51, 52].

$$2\,AlF_3\,(g\text{ or diss}) + 3\,H_2O\,(g\text{ or diss}) = Al_2O_3\,(s\text{ or diss}) + 6\,HF\,(g) \tag{1.16}$$
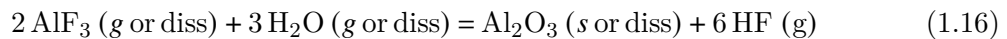
Thermal hydrolysis of pot gas

The thermal hydrolysis of the pot gas is a reaction between vaporised bath and moisture in the air stream. At the operating temperature of the cell, the major vapour fluoride species from the molten electrolyte is $NaAlF_4$ [40, 56] (Most volatile species evolved is $NaAlF_4$ [17]).

Aluminium fluorides in the form of $NaAlF_4$ due to vaporisation of the electrolyte [56] could react directly with air moisture [40] or with water adsorbed on the alumina surface which is released as steam when experiencing a large temperature difference [53]. The same reaction can describe the two different mechanisms, shown in Equation (1.17) [17, 33, 54].

$$3\,NaAlF_4\,(g) + 3\,H_2O\,(g) = Al_2O_3\,(s) + Na_3AlF_6\,(l/s) + 6\,HF\,(g) \qquad (1.17)$$
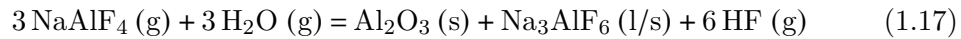
Hydrogen production methods

The hydrogen gas to be used as the reducing agent is produced by three methods, which are called grey, blue and green hydrogen [57]. The grey and blue hydrogen is produced by steam reforming, whereas the blue hydrogen utilises carbon capture technology to reduce the environmental impact [58]. Green hydrogen is produced by water electrolysis, with electricity supplied from renewable energy sources [19]. Today, over 90 % of hydrogen production is performed by steam reforming of natural gas [57]. 60 % is produced as the main product and the rest is a by-product of petroleum refining and chloralkali electrolysis [59]. Hydrogen is mentioned as a future solution to provide clean energy and energy storage, but it then requires clean electricity [57].

1.4 System description and research questions

To evaluate the potential environmental effects of the alternative production route of primary aluminium production compared to the conventional route, a Life Cycle Assessment (LCA) has been developed. The assessment is performed by studying the production routes' impact from raw material acquisition, production, transport and use to the end-of-life treatment, to provide a robust comparison between the studied systems.

The main issue with the LCA method is that the inputs and outputs are aggregated into impact categories using assumptions and uncertainties associated with each material or energy flow, accumulating considerable uncertainty for each impact category. The LCA study must consider these uncertainties to provide a robust and correct result.

The application of the LCA methodology for the study of the primary aluminium production routes is described in more detail throughout Chapter 3.

The main goal of this thesis is to investigate the environmental performance of primary aluminium produced by the use of hydrogen diffusion anode, and the main objectives are:

- To develop a system description and a model for process simulation of the primary aluminium production process, for the conventional approach using a carbon anode and a novelty approach using a hydrogen diffusion anode.
- To develop the LCA of the primary aluminium production process, comparing the two alternative approaches to identify main differences and important contributions.

- To investigate the effect of a change in the electricity mix, fuel sources and hydrogen production methods on the environmental impacts of primary aluminium production.

The main goal and objectives lead to the following research questions:

- What are the life cycle characteristics of the primary aluminium production, using consumable carbon anode and hydrogen diffusing anode, in Norway, and the different impact contributions from the two alternative production routes?
- How sensitive is the environmental impact of aluminium production to fuel sources, reductant production method and changes in the electricity mix?

A simplified flowchart of the two systems and the main reactions occurring in the reduction cell is illustrated in Figure 1.4 on the next page.

System 1: Conventional aluminium production process with **consumable carbon anode**

Carbon reductant

Electrolyte

Electrochemical reduction cell:

$Al_2O_3 + 3\,C = 2\,Al + 3\,CO_2$

Emissions and by-products

Liquid aluminium

System boundaries

System 2: Alternative aluminium production process with **hydrogen diffusion anode**

Hydrogen reductant

Electrolyte

Electrochemical reduction cell:

$Al_2O_3 + 3\,H_2 = 2\,Al + 3\,H_2O$

Emissions and by-products

Liquid aluminium

System boundaries

Figure 1.4: Simplified flowcharts of the two primary aluminium production systems, with main chemical reactions.

This thesis is structured in the following way:

- In **Chapter 1: Introduction** the life cycle of primary aluminium production process has been described, and the hydrogen fluoride evolution mechanisms are explained. The aim, objectives, research questions, system description and the use of an LCA for this study have been described.

- In **Chapter 2: Previous work and future trends** previous studies regarding primary aluminium production and the use of hydrogen as reducing gas is identified and discussed. The future prospects for aluminium and hydrogen demand and production are described.

- In **Chapter 3: Material and methods** the methodological choices for developing the Life Cycle Assessment are described, including the definition of the goal, the functional unit, the system boundaries and the impact categories to be assessed.

- In **Chapter 4: Results and discussion** the impact assessment and contribution analysis results are presented and discussed, together with the sensitivity analysis.

- In **Chapter 5: Conclusion** the main findings of this study is stated.

Chapter 2

Literature review

2.1 Conventional production route

The environmental impacts of the conventional aluminium production route are thoroughly studied. Numerous reports are available, both from industry and researchers. The International Aluminium Institute (IAI) reports that electricity production is the most significant contributor to overall environmental impact globally, contributing between 50 % and 90 % of the environmental impact in almost every impact category [60]. The most significant contributors to GHG emissions are the calcination of bauxite ore to produce Al_2O_3 and the electrolysis process. Electricity emissions contribute around 65 % to GHG emissions, while direct process emissions contribute 14 % [60]. The International Energy Agency (IEA) further emphasises this, stating that aluminium oxide refining and smelting account for over 90 % of the emissions [61]. The IAI report concludes that the power mix is the most significant influence on primary aluminium production, highlighting that a high share of hydropower results in greater contribution from process emissions, while a high share of thermal power from fossil fuel results in electricity as the most significant contributor [60].

The IAI published a report on the future roadmap for the aluminium industry and concluded that decarbonising electricity offers the most significant potential for GHG emissions reduction of the global aluminium sector [6]. Regarding the direct process emissions, the need for zero-emission technologies for heat, electricity and direct cell processes was concluded [6]. Research into the hydrogen diffusion anode as an alternative for reducing direct carbon emissions is presented in the next section.

Shahjadi et al. [62] confirmed the life cycle findings provided by the IAI [60] regarding the main impact categories for conventional primary aluminium production. Namely, global warming, human carcinogenic and non-carcinogenic toxicity, acidification, freshwater ecotoxicity and fossil resource scarcity. The results were consistent with the previous industry-provided report, that power consumption in the smelting process and calcination in the alumina production are the two main contributors to environmental impacts [60, 62].

2.2   Hydrogen diffusion anode

One of the proposed solutions to the GHG emissions from the consumable carbon anode is to use hydrogen as an oxidisable gas to depolarise the anode process reducing gas [34]. An added bonus of using a depolarising gas is that it will lower the anode potential and hence the energy consumption [35].

Mokkelbost et al. [33] studied the use of a depolarising gas anode and found that in general, the presence of water in some form promotes the formation of HF gas [33]. This is found in multiple studies regarding hydrogen fluoride generation in a reduction cell [40, 53].

Namboothiri et al. [37] also predicted high HF emissions, and found that the carbon can be replaced by a high-temperature material, such as nickel, for gas diffusion, as proposed in other studies [33, 35].

Patterson et al. [53] studied the effect of the hydrogen content in the anode on HF formation. They found that "any reduction of hydrogen content in the anode should lead to a direct reduction in the overall emissions" [53]. Increased hydrogen content in the process increases the H_2O content in the cell and hence the HF formation [54].

Wahsniedler et al. [51] studied a 170 kA prebake cell, with an anode hydrogen content of 0.093 %, and found that the fraction of hydrogen converted is around 8 %, a factor that is widely used [40].

Patterson et al. [53], studied a 170 kA, point-fed cell with an anode hydrogen content of 0.044 wt%, and found that up to 10 % of the anode hydrogen content reacts to form HF, which makes up around 8 % of the total HF emissions of the cell.

The presence of water promotes HF formation, while the direct reaction with H_2 yields less HF, since H_2 is more noble than Al so the re-dox reaction is forced to the left [33]. By simple stoichiometric for the aluminium electrolysis process with hydrogen anode, the amount of H_2 needed to produce 1 329 kg (1 t Al = 112.08 kg) is 148.96 kg, producing 1 331.12 kg gaseous H_2O (1 t Al = 1 001.53 kg). When we consider the fact that roughly one-third of the H_2O is converted to HF, while the H_2 yields less HF, then it is easy to see that the HF emissions are likely to increase with the introduction of hydrogen to the cell [33].

Chapter 3

Materials and methods

3.1   Life cycle assessment methodology

A Life Cycle Assessment (LCA) is a tool to quantify the potential environmental impacts of a product system throughout its life cycle [63]. The life cycle of a product includes the raw material acquisition, production process, product use and waste management [64], and the methodology is used to identify the most important environmental impacts and the contributors to these [63]. The benchmark standards for constructing an LCA are the ISO standards ISO 14040 and ISO 14044 [65], and the methodology is widely applied in practice [66].

ISO14040 and ISO14044 describe the LCA procedure, which consists of four phases [64] as illustrated in Figure 3.1, which are introduced and further explained throughout this chapter.
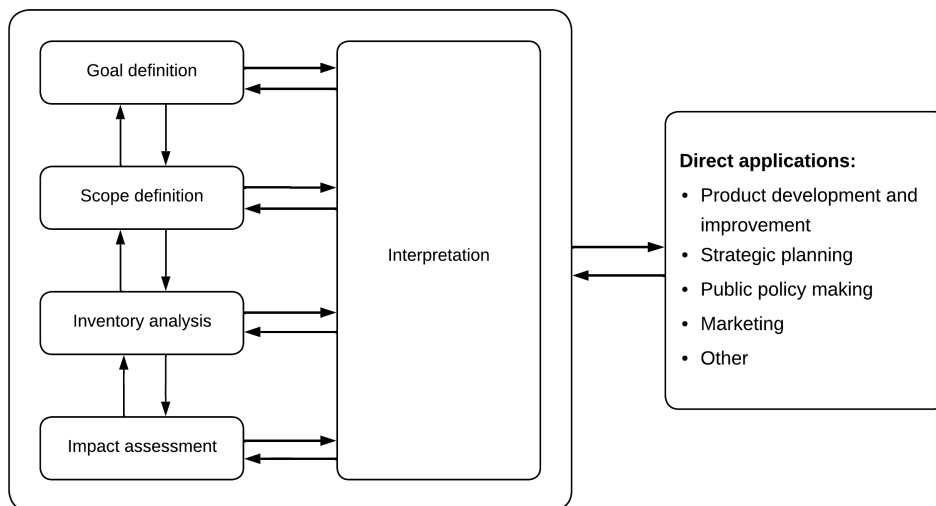
Figure 3.1: Illustration of the LCA methodology and the four phases, from ISO14040 [64]

3.2   Goal and scope

In the goal and scope phase of an LCA study, the purpose of the study and an outline of how the study will be performed should be clearly described [67]. The scope definition should explain the system of the study and the methodological choices, assumptions and limitations [68].

3.2.1   Goal definition

The present study aims to quantify and evaluate the environmental impact of producing aluminium using a hydrogen diffusion anode, compared to using a consumable carbon anode in the conventional production method. The analysis aims to identify the main environmental impacts of the process, and where in the cycle these occur. In addition, this study aims at identifying key areas of the system where available data is of insufficient quality. The intended audience of this study is aluminium industry actors, metallurgical researchers and other research organisations.

3.2.2   Scope definition

Functional unit

The functional unit (F.U.) is a quantitative measure of the function that the product or system provides and must be chosen to facilitate easy comparison of different production routes [66]. The F.U. is the reference to which all inputs and outputs are related and needs to be of similar qualities for both systems to be comparable [67]. The input to the system is Al_2O_3 and H_2 or C, and the by-products of the process are CO_2 or H_2O. Both systems produce liquid aluminium, the difference between the two production processes is the anode material, yielding different off-gas compositions. The main input of Al_2O_3 and the main output of Al is unchanged, so to compare the function of the systems 1 tonne of liquid aluminium is chosen as the functional unit. All environmental performance indicators are normalised to the functional unit.

Type of LCA and handling of multifunctionalities

Identifying the most suitable type of LCA, or modelling framework, is imperative to the quality of an LCA study and highly depends on the purpose of the study [66]. This is important for the methodological choices to be made, regarding system boundaries, allocation procedures and data choices [69]. There are two different types of LCA, the attributional LCA (ALCA) and the consequential LCA (CLCA), also referred to as descriptive (accounting) and change-oriented respectively [70]. In short, a CLCA accounts for the change in global impacts of a product life cycle as a direct or indirect consequence of a decision, while an ALCA accounts for the share of the global impact linked with the isolated product life cycle [66, 70]. This distinction is illustrated in Figure 3.2 [71].
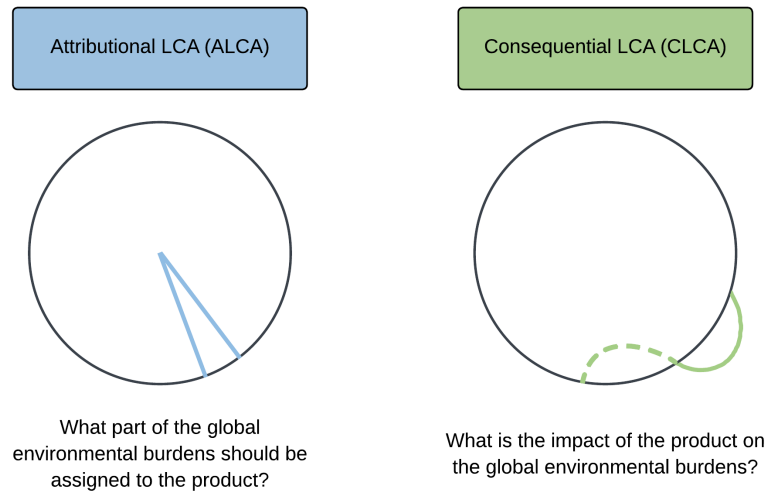
Figure 3.2: Illustration of the difference between attributional and consequential LCA, from Weidema [71]

While a CLCA is concerned with the broader environmental consequences of individual decisions, the ALCA tries to avoid connections to large systems with large environmental impacts [72]. The system in this study has a process-specific focus, trying to have a confined, concise and correct system, isolated from the less relevant processes outside of the system. For the present study, an ALCA would identify the environmental impacts attributed to the liquid aluminium as a stand-alone product, not considering how the change in the production process affects other processes or products outside of the system boundaries, such as hydrogen demand or petroleum waste recycling used in the prebaked anodes.

Average data is used in an ALCA and represents the average environmental impact of the actual physical flows in the system for producing a unit of the product [66]. Marginal data is used in CLCA and represents the effects of small changes in the output of the system product on the environmental impacts of the system [66].

An attributional LCA is a more technical descriptive analysis, studying the cause and effects of the processes and process chains of a product or system. It is suitable to identify the connections between the system and the potential environmental impacts, and how the different flows and unit processes affect the impact of the product, and is illustrated from Figure 3.3 on the next page.

ATTRIBUTIONAL LCA

Inventory (LCI)

Impact assessment (LCIA)

— Product → Human / industrial product system → Elementary flows → Environmental system → Environmental impact →
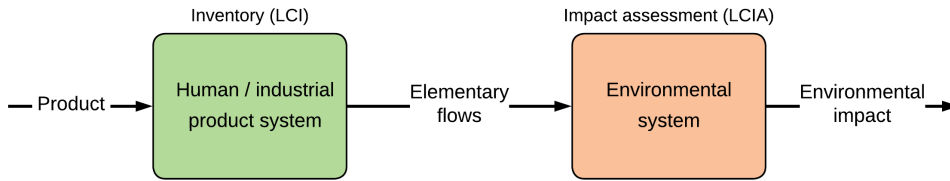
Basic formula: *Product amount* *x* *linear factor* *=* *environmental impact*

CONSEQUENTIAL LCA

LCI and LCIA could be fully integrated

— Product → Human / industrial product system | Environmental system → Environmental impact →
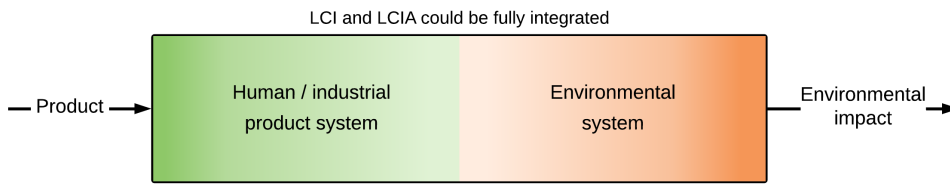
Basic formula: *Function(decision)* *=* *environmental impact*

Figure 3.3: Illustration of the mathematical difference between attributional and consequential LCA, from Schaubroeck et al. [73]

Hydrogen diffusion anode is not technologically mature enough to be implemented in a large-scale system and requires further experimental research and pilot testing [37]. Data on the consequences of substituting carbon anode with hydrogen diffusion anode is scarce, and will not be suitable for making assumption choices regarding the consequences of implementing the change. This study will be more useful as a process-specific study, aiming to be as accurate as possible with the available data and assumptions made.

In the LCA community, there is a disagreement regarding the correct method of performing an LCA study, but there have been made arguments that both ALCA and CLCA can be used for decision-making and for learning purposes [66]. There has also been discussion regarding past and future systems, but there has been argued that both ALCA and CLCA can be used to evaluate past and future systems [66, 72]. Many LCAs are incorporating both ALCA and CLCA in the same study, to complement each other and obtain a robust result [74].

The alternative system in this study inhabits these characteristics, aiming at assessing a future production alternative, with only a few preliminary laboratory experiments performed, and in the need of experimental research and pilot testing before it could be implemented at a larger scale. An ALCA is suitable to use when the production systems are not applied at a large scale, since the consequences of the production are less important at a smaller scale, due to the lower amount of materials and energy used.

A consequential LCA for the system of study would investigate how introducing the hydrogen diffusion anode to the production process would affect other activities in the market. Hydrogen is a part of the "green transition" [75], and the use of hydrogen in aluminium production prevents it from being used in petroleum refining or fertiliser production. Hydrogen produced today is almost entirely supplied from fossil fuels [57], and this demand will increase with the change to hydrogen in the aluminium smelter industry. A consequential LCA would account for the increased global demand for hydrogen, and hence fossil fuel consumption. In an even broader understanding, the increased demand for hydrogen might affect the passenger car market, by slowing down the research and introduction of hydrogen as fuel, due to a possible shortage in the hydrogen market.

For this study, in compliance with the stated goal and scope, it is of interest to see how the change in process input affects the environmental impacts of the production of 1 tonne of liquid aluminium. The broader consequences for the rest of the hydrogen consumers are not within the scope of this study. The system of study is at the early R&D stage, and this study aims at providing a preliminary result on what changes one could expect by changing the input from carbon to hydrogen. Hence the broader consequences for other hydrogen consumers are not of interest until the process under study has been further researched and implemented at a larger scale.

Handling of multifunctionalities

During the modelling of the inventory, multifunctionalities of the system might be encountered. An LCA's multi-functionality is when a process has multiple inputs or outputs, or where processes are shared with other product systems [67]. These multi-functionalities should be treated through the step-wise allocation procedure as defined in ISO14044 [68]:

1. **Avoid allocation by subdivision**: Dividing the unit process into smaller sub-processes to obtain specific impacts, input and output data to separate the production of product from co-product. The system in this study, the production of liquid aluminium consists of multiple interdependent chemical reactions needed to obtain correct bath and electrolysis conditions to result in the final product, meaning that the sub-division method is unsuitable for this study.

2. **Avoid allocation by system expansion**: Expanding the system to include the additional functions of the by-product, where the environmental impacts of the alternative production process of the co-product are added to or subtracted from the initial system.

3. **Allocation**: Dividing (partitioning/allocating) the inputs and outputs of the system and assigning (allocating) them to each of the products based on physical or non-physical relationship, such as mass or economic value.

Subdivision and allocation narrow the system, making it more focused, while system expansion enlarges the system [66]. A proposed solution is to substitute by system expansion, also called avoided burden method, where the environmental burden of an alternative production process is added or subtracted from the initial system [76].

This study aims at comparing two production processes of the same product, to see how the change in input and off-gas composition impacts the environment. Alumina reduction using a consumable carbon anode is the reference system, while the modified process using a hydrogen diffusion anode is the alternative system. For the off-gas, the study will investigate how reduced CO_2 emission and increased HF emission impacts the environment.

For the system in the present study, the production process of HF is the alternative production process, which is included as a by-product in the expanded system, illustrated in Figure 3.4 in the next section.

System boundaries and limitations

This study aims at comparing two production processes of the same product, to see how the change in input and off-gas composition impacts the environment. Alumina reduction by the use of a consumable carbon anode is the reference system, while the modified process using a hydrogen diffusion anode is the alternative system. For the off-gas, the study will investigate how reduced CO_2 emission and increased HF emission impacts the environment.

In the conventional production route, the carbon anode is oxidised by the Al_2O_3 to produce liquid aluminium, with CO_2 as a by-product. Part of the carbon is removed from the cell unreacted, as the consumed anode is replaced with a fresh anode, called anode butts in the figure. As explained in Chapter 1.2, some amount of HF is produced with carbon as a reductant, mainly due to moisture in alumina, hydrogen content in the carbon anode and air moisture. The main difference between the two systems is that the conventional system produces mainly CO_2 as waste emission, while the alternative system produces an increased amount of HF. The difference is illustrated in Figure 3.4 as blue arrows for the carbon route and yellow arrows for the hydrogen route. As seen in the figure, the HF is captured and recycled in the conventional system, and is included as an avoided burden.

System 1: Conventional aluminium production process with **consumable carbon anode**
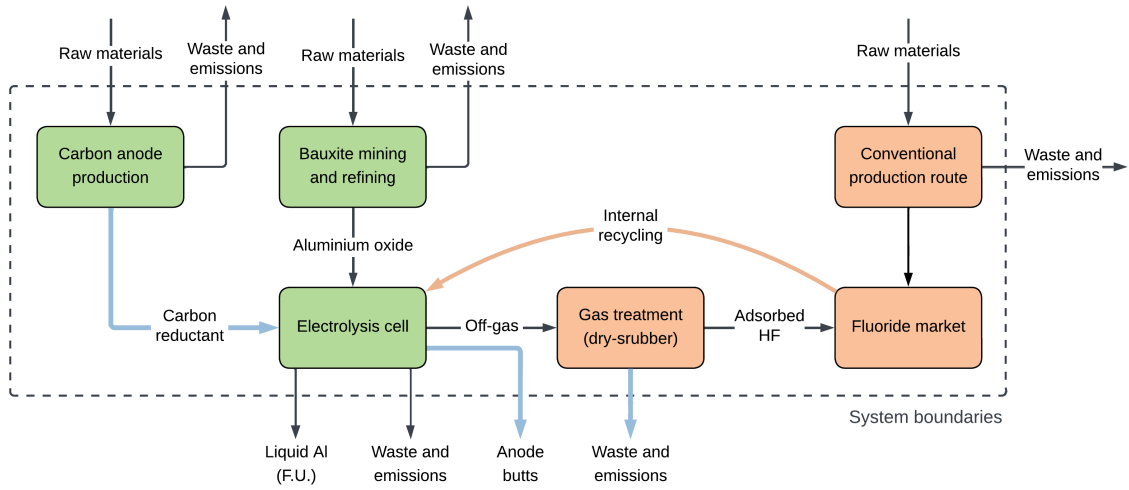
System 2: Alternative aluminium production process with **hydrogen diffusion anode**
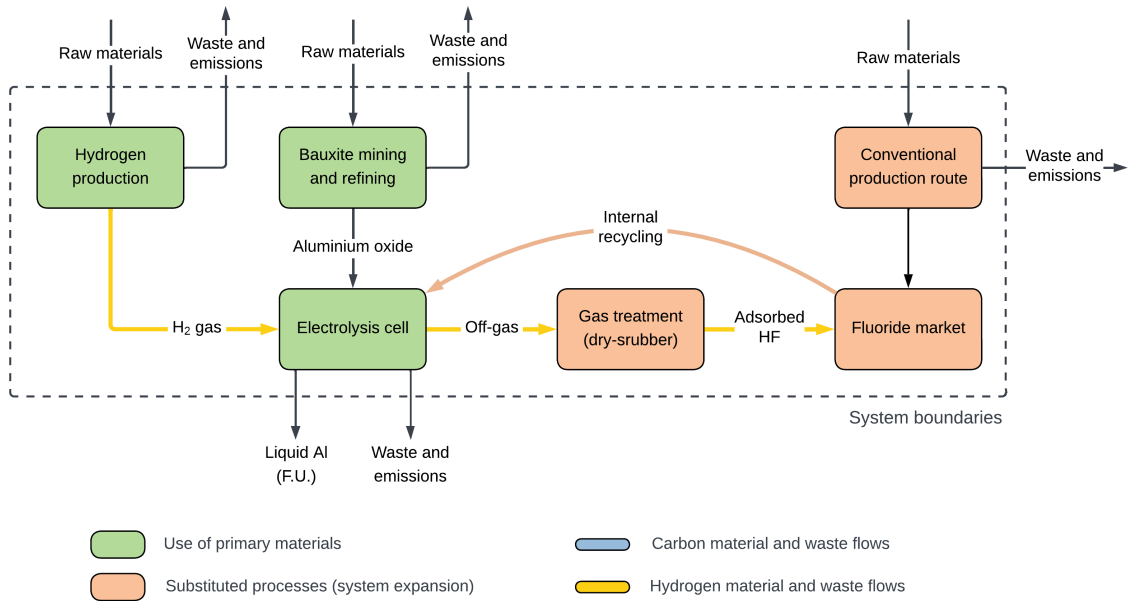
Figure 3.4: Flowcharts of the expanded systems

The main goal of this study is to compare the emissions of two production processes, altering one input and keeping all other parameters unchanged. So the significance of chosen spatial boundary is low, but to make the study more realistic, Norwegian conditions are considered in this study. Subsequently, if data from Norwegian conditions are unavailable, the data is assumed to be similar to average European conditions.

Impact categories, methods and software tools

The impact methodology used in this study is the ReCiPe 2016 (H) method, at both midpoint and endpoint, by the National Institute for Public Health and the Environment (RIVM) of the Netherlands [77]. The hierarchist view is used in this study because it is a balanced approach between the short-term perspective of the individualistic approach and the long-term perspective of the egalitarian approach [77], and is the model used in most scientific research [78]. The LCA software SimaPro is used in this study, where the ReCiPe methodology is incorporated in the ecoinvent LCI database used in SimaPro.

Characterisation factors are used to convert elementary flows, the resources, emissions and wastes, of similar characteristics into impact categories[78]. As illustrated in Figure 3.5, the characterisation factors at the midpoint level group the inputs and outputs into environmental impacts, which again are grouped into damage pathways, resulting in the endpoint indicators [77].
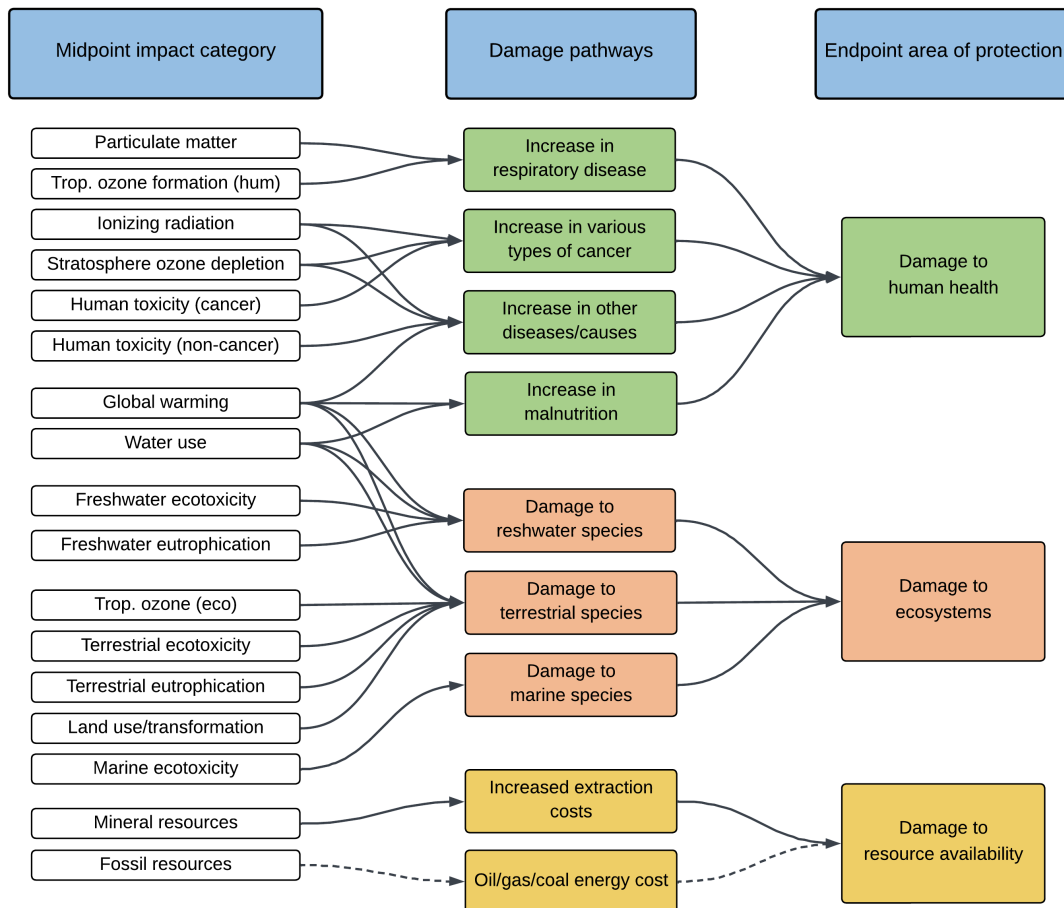
Figure 3.5: Schematic illustration of the impact categories, pathway and endpoint area of protection of the ReCiPe methodology [77].

Whereas the midpoint categories focus on single environmental impacts, the endpoint indicators, or Areas of Protection, present the environmental impacts at a higher aggregation level. Converting and grouping the midpoint impacts into three endpoint impacts makes the LCIA results easier to interpret, but at the same time, the uncertainty increases with each aggregation step, grouping multiple uncertainties together. By using endpoint impact categories, the detailed analysis is lost, and hence to account for the detailed pathway and to provide an easily interpreted result, both midpoint and endpoint analysis should be assessed [78].

The impact categories to be investigated are global warming, ionising radiation, ozone formation (human health and terrestrial ecosystems), particulate matter formation, terrestrial acidification, eutrophication (freshwater and marine), ecotoxity (terrestrial, freshwater and marine), human toxicity (carcinogenic and non-carcinogenic), land use, resource scarcity (mineral and fossil) and water consumption. A brief introduction to the impact categories considered is presented below:

Global warming: The Global Warming Potential (GWP) express the GHG emission's capacity to absorb infrared radiation, resulting in increased atmospheric temperature, and is expressed in kg $CO_{2eq.}$. GWP is associated with the endpoints of human health and damage to ecosystems.

Ozone formation (human and ecosystem): Ozone is harmful depending if it is present in the stratosphere or troposphere. The stratospheric ozone creates a protective layer which reduces the harmful UV radiation reaching the Earth's surface, while the tropospheric ozone negatively affects the respiratory systems and plant biomass. Tropospheric ozone is produced by photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NOx). The ozone formation potential of a substance is expressed in kg nitrogen oxide equivalents ($NOx_{eq.}$). As mentioned, this impact affects the endpoint of human health and damage to ecosystems.

Fine particulate matter formation: Fine particulate matter formation is air pollution causing aerosols in the atmosphere and is expressed as kg $PM_{2.5eq.}$ (kg of particle matter of size less than 2.5 µmeter). These particles can be inhaled and cause increased mortality and damage to the human health endpoint (Years of Life Lost).

Freshwater and marine eutrophication: Eutrophication is when the environment experiences excessive levels of nutrients, mainly phosphorous and nitrogen for freshwater and marine eutrophication respectively. This causes aquatic plant overgrowth resulting in reduced water quality and decreased biodiversity. Freshwater eutrophication is measured in kg P equivalent and marine eutrophication in kg N equivalent and causes damage to ecosystems.

Toxicity (carcinogenic, non-carcinogenic, freshwater, terrestrial and marine): The Toxicity Potential (TP) express the potential harm of chemicals released into the environment and is expressed in kg 1.4-dichlorobenzene equivalents (1.4-$DCB_{eq.}$). The different toxicity categories are calculated through an environ-

mental fate factor, an exposure factor, a toxicity effect factor and a toxicity-effect damage factor. These represent the distribution and transformation of chemicals in the environment, connects the chemical masses to human exposure or the dissolved chemicals, indicates the potential toxicity effects per chemical mass and relate the potential effects to the endpoints of damage to human health or ecosystems.

Terrestrial acidification: The Terrestrial Acidification Potential (TAP) expresses the changes in soil chemical properties due to deposition of acidifying chemicals, mainly nitrogen and sulphur, and is expressed in kg sulphur dioxide equivalents ($SO_{2eq.}$). Acidification results in declined soil fertility, a decrease in root production and a reduction of photosynthetic rates, causing damage to damage to ecosystems.

Resource scarcity: Mineral resource scarcity represents the consumption of virgin mineral material, and the extraction of aggregates, metal ores and minerals causes a decrease in the ore grade. The actual and expected future extraction is compared to the future extraction of 1 kg copper (Cu) by the characterisation factor Surplus Ore Potential (SOP), and is measured in kg Cu equivalents. Fossil resource scarcity is the ratio between the energy content of the fossil resource and the energy content of crude oil. This impact is expressed as kg oil equivalent, and both resource scarcity impact categories cause damage to resource availability.

Ionising radiation: The Ionising Radiation Potential (IRP) accounts for the anthropogenic emissions of radionuclides, from the nuclear fuel cycling, burning of coal and mining of phosphate rocks. It is expressed relative to the emission of reference substance Cobalt-60 to air with the unit kBq Co-60 $_{eq.}$ and causes damage to human health in disability-adjusted life years (DALY).

Data quality requirements

To obtain a robust and precise assessment, the data should be representative of spatial, temporal and technological coverage in compliance with the system boundaries as defined in the scope of the study. Data for the foreground system is modelled by the use of scientific reports and process simulation. The aim is to use the best possible data available, either from experimental research or stoichiometric considerations. The background data is provided by the comprehensive ecoinvent LCI database. The version used in this study is the 3.6 version from 2019, meaning the background data is not necessarily the most up-to-date data available. This might add uncertainties to the results, but the data is still recent, and the uncertainty will be assessed in Chapter 4.3.

The inventory and assumptions made are developed throughout Section 3.3.

3.3   Inventory analysis

During the Life Cycle Inventory (LCI) phase of an LCA, the inputs and outputs required to produce the functional unit of the system are identified and quantified, in compliance with the defined goal and scope [76]. To obtain robust and detailed results, the system of study is modelled by two different systems, the foreground and background systems. The foreground system describes the specific data for the system of study, the materials and resources required for the system, and the resulting products, byproducts, emissions and waste. The background modelling describes the value chains upstream of the defined system, and is modelled using generic data from an LCI database.

3.3.1   Foreground modelling

To model the system consisting of a comprehensive amount of chemical reactions facilitating other side reactions, several assumptions and simplification has been made. A mix of literature analysis and process simulation has been made, and the main assumptions and limitations of this study are presented in this section. Many factors of the system in the study are dependent on operation procedures, hence a mix of literature data, laboratory experiments data and stoichiometric considerations have been used in this study.

All material flows are normalised to the functional unit of 1 tonne of aluminium, and the multi functionalities of the system have been treated by expanding the system by substitution, the Allocation at Point of Substitution (APOS) system model. The considerations and assumptions made are described during the continuation of this chapter, together with tables of the full inventory of the studied systems.

The electrochemical reduction process of Al_2O_3 to aluminium is well-established, with several studies and industry-provided descriptions of the process and energy and mass balances available. The process consists of numerous different reactions, where some are intermediate reactions acting as facilitators for other reactions. As an example, the dissolution of Al_2O_3 to facilitate the reduction of aluminium at the cathode and oxidation at the anode is done through multiple reactions. The alumina feed, carbon anode and electrolyte input to the cell and the CO_2, HF and liquid aluminium out of the cell account for the overall chemistry in the reaction. This means that only the flows crossing the system boundaries are considered, while the intermediate reactions are either balanced for or decided to be outside the scope of the study.

The aluminium production system of this study is assumed to exist in an averaged steady state condition, a mature cell older than 1 000 days. The electrolysis cell experience reduced AlF_3 requirements due to the extensive uptake of Na in the cathode during the early operational life, which are countered by the addition of Na_2CO_3. The continuing Na uptake of a mature cell due to temperature gradients down the side ledges is less than 1 % of the overall consumption [26], and is not included in the system of study. For a steady-state cell, the short-term fluctuations in temperature, bath composition, reaction rates and HF evolution due to anode change and point feeding of alumina are not considered. The end-of-life treatment and re-lining of the cells are not considered,

and the anode effect and the resulting evolution of C_2F_6 and CF_4 are not considered. These emissions have high global warming potentials but are produced irregularly when the Al_2O_3 concentration of the bath becomes too low and the voltage increase rapidly. The cell chemistry of a stable cell represents the described cell reactions in Chapter 1.2 most accurately.

The mass and energy balance has been constructed primarily using data from literature, and evaluated in the chemical process simulation tool HSC Chemistry. When literature data has been deemed inadequate, stoichiometric calculations have been used. A stable cell using literature and stoichiometric considerations is believed to result in the most accurate mass and energy balance.

The temperatures used to obtain the energy balance are found in literature as mentioned in Chapter 1.2, where the room temperature is 25 °C (298 K), and the operational temperature is 960 °C (1 233 K) [10, 19].

A cell voltage of 4.1 V and current efficiency of 94 % has been assumed to express an industrial cell [18]. The specific energy consumption of the cell has been calculated to be 13 MWh/t Al from Equation (1.2) in Chapter 1.2. This amount is lower than the global average of 14.1 MWh/t Al [11], but higher than Hydros best-performing smelter at 12.3 MWh/t Al [79], and has been decided to act as a suitable midpoint between current and future energy consumption.

All the carbon consumption reactions are accounted for in the net carbon input of 425 kg [10], including the air burn, Boudouard reaction and unreacted anode butts, and the overall reaction provides a good estimate suitable for the scope of this thesis. In addition, all CO produced is assumed to burn to form CO_2 under the hood, hence the ratio of CO to CO_2 is not relevant to the scope of this thesis.

For the carbon anode, a residual hydrogen content of 0.094 wt %, amounting to 4 kg/t Al, with a conversion factor of 10 % [51, 53] is assumed. Due to a lack of experimental data on the use of hydrogen as a reducing gas, the amount of hydrogen used in the hydrogen diffusion anode system is calculated stoichiometric from Equation (1.11) in Chapter 1.3. This amounts to 112 kg/t Al, and an equilibrium conversion of H_2O to HF of 35 % is used in this study, a simplified midpoint between the 40 % of Wahnsiedler et al. [51] and the one-third of Mokkelbost et al. [33].

The remainder of the unreacted hydrogen either forms part of the dissolved water content in the bath or is transported to the extraction system via the crust vents where it could aid in secondary HF generation [53]. These mechanisms are not considered due to inadequate data, only the main HF generation from the anode hydrogen content is included in the study.

The aluminium oxide input is assumed the stoichiometric value of 1 889 kg/t Al, which is assumed 100 % reacted to form aluminium in the cell. The structural water and moisture content of the Al_2O_3 is assumed to be similar to that of smelter grade alumina (SGA), which is normally 2.25 wt% [52] and a hydrogen conversion rate of 10 % [51, 54].

The modelling focuses on the hydrogen and fluoride species of the cell, thus the impurities of Al_2O_3, CaO and Na_2O, are not considered. The aluminium fluoride required to neutralise these impurities is not included in the mass balance, only the AlF_3 required to maintain the bath ratio is used as input, amounting to 2.25 kg/t Al [30].

As mentioned in Chapter 1.3, the AlF_3 is consumed through multiple different mechanisms such as vaporisation of bath, hydrolysis of the bath to HF by hydrogen introduced as moisture in the anode, alumina or air [51]. The two main mechanisms by which AlF_3 leaves the cell during the electrolysis, is by emission or by neutralisation by impurities in Al_2O_3 [29]. The emissions are both particulate AlF_3 and gaseous HF [40].

Input for the AlF_3 is chosen to be 2.25 kg per tonne Al, since the neutralised AlF_3 don't directly contribute to the evolution of fluoride gases. The resulting CaF_2, Na_3AlF_6 and Al_2O_3 products are dissolved in the bath, contributing with increased amounts of F, which may increase the rate of reaction for other mechanisms, but the info is scarce, and for this thesis, it is viable to neglect these possible reactions. Only 2.5 % of the CaF_2 in the bath is measured in the off-gas [51]. Calcium can only be part of the off-gas as entrained particulates, due to the absence of volatile compounds at bath temperatures [51].

The simulation model consists of fewer chemical reactions compared to the real electrolysis process. There are a vast amount of reactions that facilitate other reactions, intermediate reactions, side reactions, etc. which are neglected when not affecting HF or CO_2 emissions. The full list of chemical reaction equations used to perform the mass and energy balance is provided in Appendix B.

Table 3.1: Inventory for the electrolysis with carbon anode in SimaPro per F.U.

Output		
Liquid aluminium	1 t	F.U. of the system
Inputs		
Aluminium oxide	1.889 t	
Cryolite	0.018 t	
Aluminium fluoride	0.002 t	
Prebaked carbon anode	0.425 t	
Anode hydrogen content	0.004 t	
Electricity	13 MWh	
Emissions to air		
Carbon dioxide	1.56 t	
Hydrogen fluoride	0.018 t	

Table 3.2: Inventory for the electrolysis process with hydrogen diffusing anode in SimaPro per F.U.

Outputs		
Liquid Al	1 t	F.U. of the system
Hydrogen fluoride	0.80 t	
Inputs		
Aluminium oxide	1.889 t	
Cryolite	0.018 t	
Aluminium fluoride	0.002 t	
Hydrogen	0.112 t	
Electricity	13 MWh	

The inventory with full names from ecoinvent are found in Tables C.1 and C.2 in Appendix C.

3.3.2   Background modelling

The background system comprises all the raw materials, construction and production processes, markets and energy sources, and accounts for up to 99 % of the unit processes in a product system [80]. The database used in this study is the ecoinvent LCI database, a very comprehensive database consisting of more than 10 000 interconnected flows, and contains both country-specific and regional and global average data [80] It can provide specific processes or grouped markets, average sector values, and global or geographically specific. This makes it suitable for modelling the background of a system with limited industry-specific data. The database has no strict cut-off rule, and hence it provides a dataset as complete as possible [81].

3.4   Impact assessment

The Life Cycle Impact Assessment (LCIA) is the fourth and last phase of the LCA methodology and aims to connect the LCI results to the system's environmental impacts [76]. This phase analyses the potential environmental impacts of the system in the study, expressing the inputs and outputs in terms of environmental impact. The analysis is performed to understand better the impacts caused by the system, trying to answer what part of inputs and outputs contributes to which impact category [78]. The LCIA is performed through three mandatory and three optional steps, schematically illustrated in green colour in Figure 3.6 [68, 76].
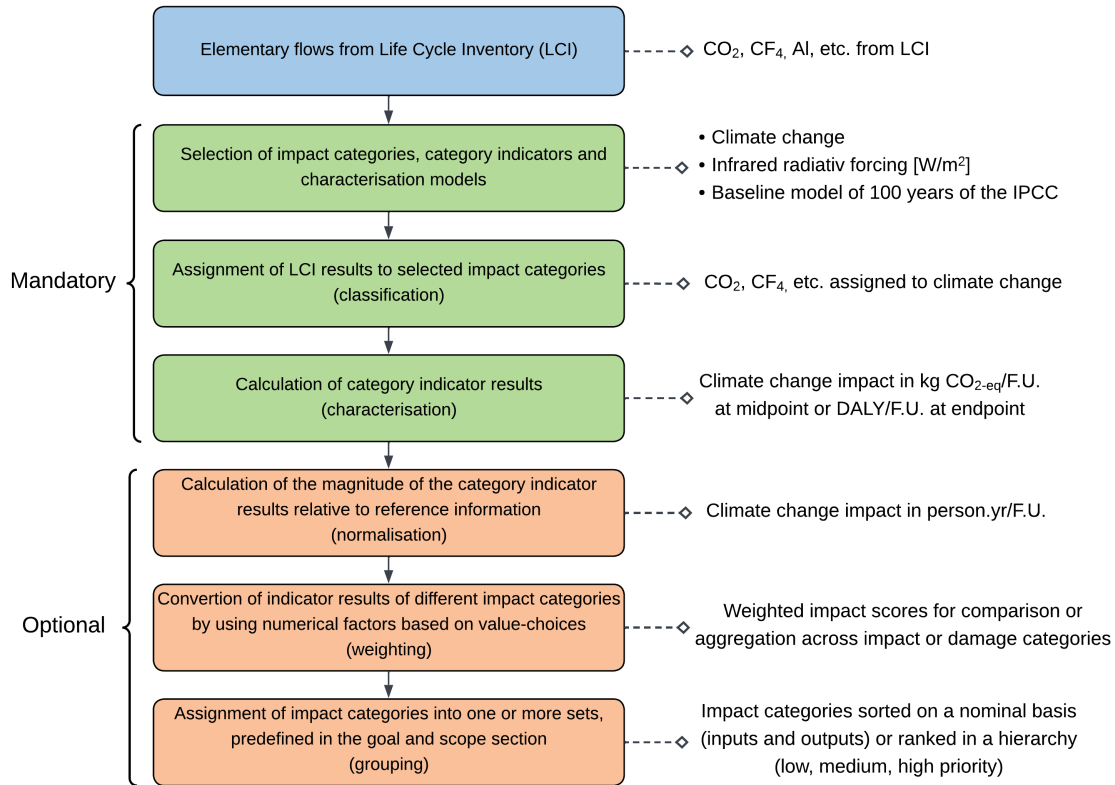
Figure 3.6: Schematic view of the Life Cycle Impact Assessment (LCIA) phases [68, 77]

The first three phases, illustrated in green in Figure 3.6, are mandatory for the LCA to satisfy the requirements in the ISO 14044 standard, while the normalisation, weighting, and grouping phases (orange) are optional [68].

The phase of selecting impact categories, category indicators and characterisation models should be consistent with the goal and scope of the study. The characterisation models are the basis of deriving the CFs and category indicators. The classification phase links the emissions to the correct impact categories. The characterisation phase calculates the relative contribution from emissions to a reference substance in the category, i.e. category indicator results. As an example, CF_4 has a characterisation factor (CF) of 6 500 kg $CO_{2eq.}$, meaning it contributes 6 500 times more to GWP than the reference CO_2. After the mandatory phases and before the optional ones, the indicator results for the different impact categories should be presented together in an LCIA profile to understand the indicator results' reliability better.

Grouping is the sorting or ranking of impact categories, while weighting is the converting and aggregating of indicator results across impact categories to reflect the relative importance of the impacts. The normalisation converts indicator results relative to a reference to understand the relative magnitude of the results. This is done by dividing

the results by a reference value, e.g. total inputs and outputs for a given area, a baseline system or per capita.

The LCIA for the system in this study is carried out using the LCA software SimaPro, using the ReCiPe 2016 (H/A) LCIA methodology, mentioned in Section 3.2.2, for midpoint and endpoint indicators. The ecoinvent database is incorporated into SimaPro, containing many existing impact categories, category indicators and characterisation factors, and the software connects the background and foreground models of the inventory.

All inputs and outputs of the system are normalised by the reference value of 1 tonne liquid aluminium, the functional unit. The impact categories evaluated and analysis methods comply with the Goal and Scope in Chapter 3.2. Normalised LCIA results for the two alternative production processes, using consumable carbon anode or hydrogen diffusion anode, are described throughout Chapter 4.

3.5   Interpretation

In the interpretation phase, the LCI and LCIA results are summarised and evaluated about the main elements of the goal and scope definition [68]. The end goal of this phase is to produce conclusions and recommendations on the indicator results' consistency to that defined in the goal and scope. The interpretation could be explained as a continuously interdependent process between all the phases of the LCA, as illustrated in Figure 3.7.
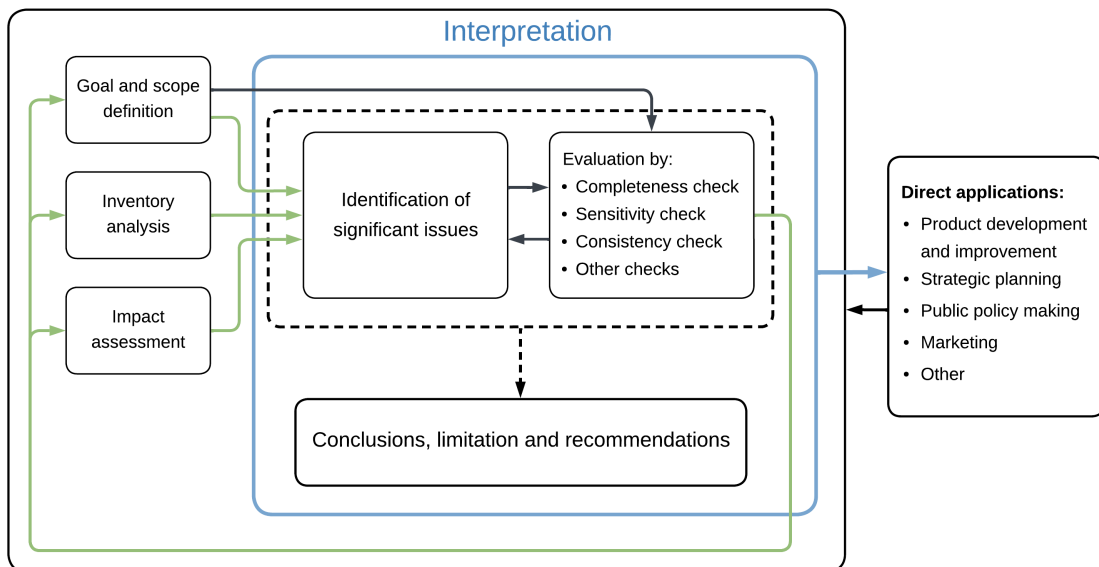
Figure 3.7: Schematic view of the interpretation phase of an LCA [64, 67]

As Figure 3.7 shows, the first step of the interpretation is to try to identify significant issues of the LCA. If the results are inconsistent with the goal and scope, it should be identified if it is because of wrong assumptions or poor data quality, resulting in a misguided/inaccurate inventory. This phase should see if the LCA is suitable for the intended application, the audience of the study and the reason for the study to be carried out. These significant issues are evaluated through one or multiple checks, namely completeness, sensitivity and consistency checks. As illustrated by the green arrows in Figure 3.7, the results of the interpretation checks are introduced to the previous LCA phases, and this iterative method continues until the results are satisfactory about the scope. Then the limitations of the interpretation phase, conclusions and recommendations are made.

Throughout the work of this study, the interpretation phase has been continuously considered to improve the quality of data and assumptions. Limitations and assumptions for this study are described in the Goal and Scope (Chapter 3.2, and the interpretation phase evaluates these.

A sensitivity analysis of the system has been performed to improve knowledge of the robustness of the result and better understand how different scenarios within the system affect the impacts and is presented in Chapter 4.3.

Chapter 4

Results and discussion

The impact results presented in this chapter are obtained by the path from the Goal and Scope definition in Chapter 3.2, through the inventory analysis in Chapter 3.3, to the impact assessment in Chapter 3.4. The LCIA evaluated the production of 1 tonne of liquid aluminium by two alternative production routes, the carbon anode and the hydrogen diffusion anode routes. The hydrogen anode system was expanded to include the hydrogen fluoride emission as a by-product for internal recycling or to the HF market. The overall impact results are presented as three systems in Figure 4.1 to show the direct effects of replacing carbon with hydrogen at the anode, and at the same time show the effect of re-using the hydrogen fluoride emissions from the smelter cell.
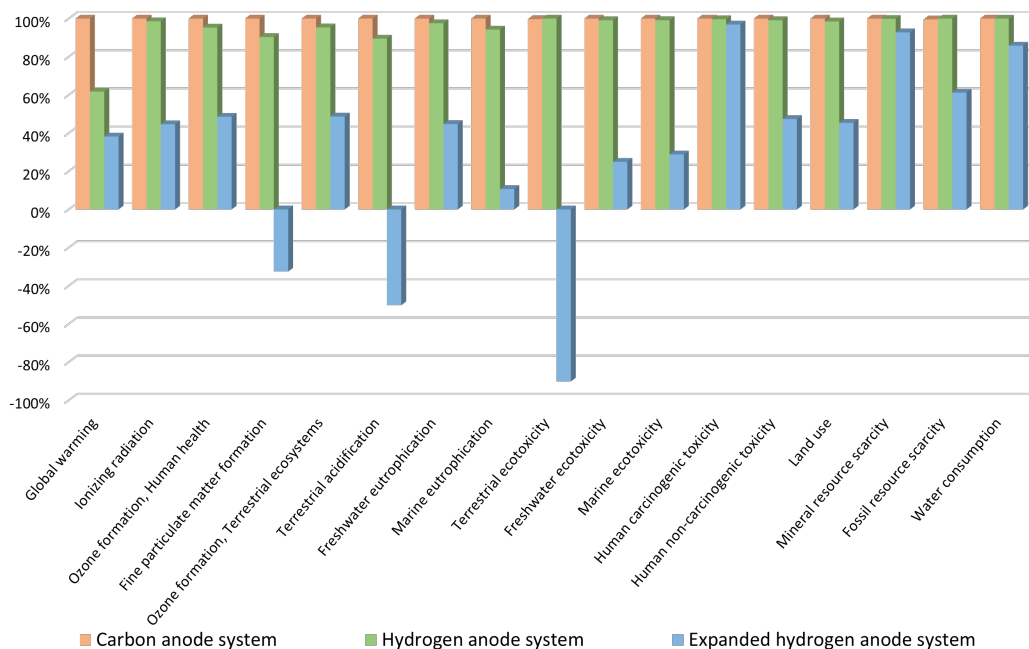
Figure 4.1: Comparison of the midpoint impact results of the carbon anode system, the hydrogen anode system and the expanded hydrogen anode system.

As seen from Figure 4.1, using a hydrogen diffusion anode affects some impact categories significantly, while some are affected very little. Half of the impact categories (9 of 18) experience less than 1 % change, while the main direct effects of changing anode material are a significant decrease in the global warming impact category and noticeable reductions in the fine particulate matter formation and terrestrial acidification impact categories. A contribution analysis has been performed to obtain a more comprehensive and detailed understanding of the impact results and identify the main contributors in the different categories. The LCIA results are analysed and described in the subsequent chapter.

4.1 Contribution analysis

In the contribution analysis, all three systems are illustrated by two columns in the graphs. As stated in each figure, the carbon anode system is to the left, and the hydrogen system is to the right. The hydrogen diffusion anode route column includes the expanded system from Figure 3.4 in the Scope definition in Chapter 3.2.2, presented as the pink blocks. During the contribution analysis, the direct effect of the change from carbon to hydrogen anode has been commented on, but the main focus has been discussing the effects of the system expansion. The total impact of the expanded system is illustrated by the black dots in the figures, which for the carbon anode route only highlights the total impact, but for the expanded system, this represents the total impact of the system, including the avoided burdens from the hydrogen fluoride by-product.

4.1.1 Global warming
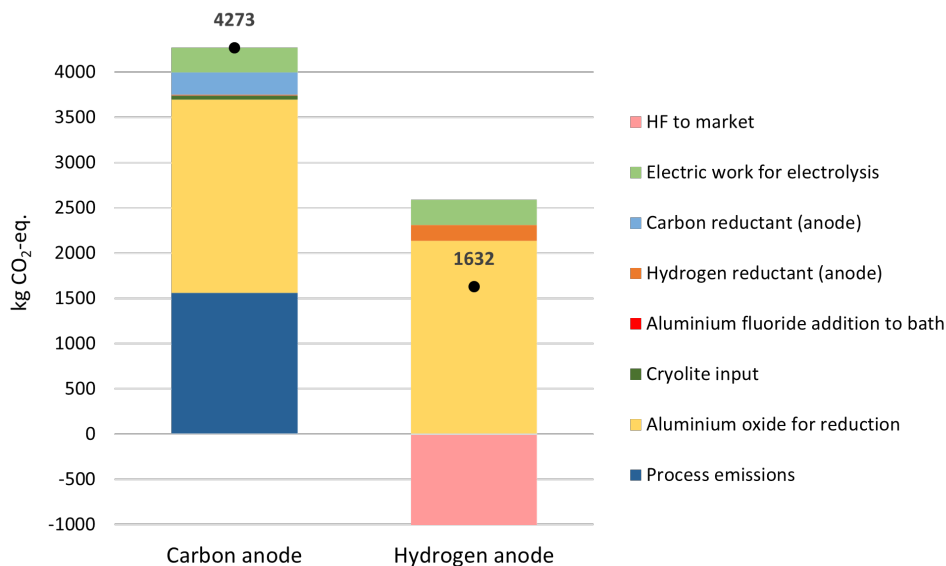
Figure 4.2: Comparison of the global warming impacts of the carbon anode system and the expanded hydrogen anode system.

Figure 4.2 shows the aluminium production routes using carbon anode and hydrogen diffusion anode and their contribution to the global warming impact category. The most significant contributor to global warming for both systems is the production of aluminium oxide, accounting for 50 % of the carbon anode and 80 % of the hydrogen anode system. This is attributed to using natural gas, heavy oil and hard coal as fuel to provide heat, mainly for the rotary kiln in the calcination process.

For the conventional production route, the direct process emissions from carbon consumption in the cell account for just above one-third of the impacts. This includes all the chemical reactions in the cell which consume carbon, mainly the reduction of aluminium oxide, air burn and the Boudouard reaction.

Prebaked anode production accounts for 6 %, whereas petroleum refinery processes, accounting for producing petroleum coke and tar pitch, contribute 25 %. The remaining impact is equally accounted for by heat and electricity production by fossil fuels, natural gas production and transport.

The direct effect of using a hydrogen diffusion anode is a 38 % reduced impact. The main contribution to GWP, other than the aluminium oxide it shares with the carbon system, is the production process of hydrogen gas. This is almost exclusively produced from fossil fuel, and the contribution accounts for around 4 % of the impacts and is the result of direct process emissions from steam reforming of natural gas and the heat required in the process.

The avoided impact from the hydrogen fluoride by-product results in a 62 % reduction compared to the conventional carbon anode system. These avoided impacts are primarily assigned to the natural gas and hard coal used to heat the oven in the HF production process. This accounts for 40 %, while electricity from fossil fuels accounts for 26 %. Sulphur production used in the chemical reaction and corresponding natural gas processes and transport accounts for around 20 %.

The electric work required for the electrolysis has the same value but accounts for 10.5 % and 6.5 %, respectively, for the carbon and hydrogen anode routes. The electrolysis process is modelled using a Norwegian electricity mix, utilising a high share of renewable energy sources. This contribution will likely increase with different spatial boundaries, with a power mix weighted more towards fossil fuels.

4.1.2   Ozone formation

The ozone formation impact of the carbon anode and hydrogen diffusion anode route are displayed in Figure 4.3 below. The ozone formation affects both human health and terrestrial ecosystems, and the two hold the same unit, they are affected by the same elementary flows, and their impact scores vary only by 1-2 %, such that they are decided to be displayed and analysed as one common impact category.
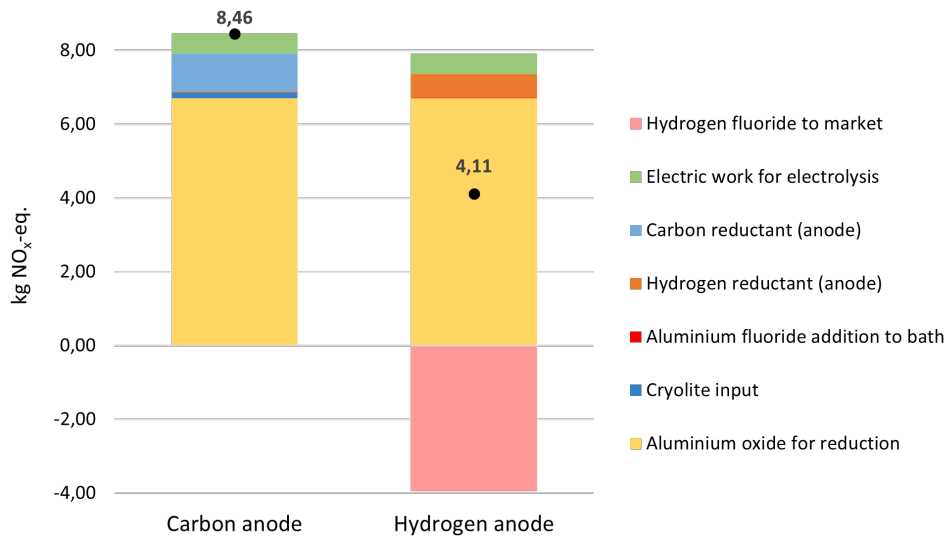
Figure 4.3: Comparison of the ozone formation impacts of the carbon anode system and the expanded hydrogen anode system.

Aluminium oxide production accounts for around 80 % of the total impact for both systems. Transport by ship and train accounts for 40 % due to VOCs from fossil fuel combustion, while the fossil fuels used for heating the calcination process account for 17 %. Burning of fossil fuels releases nitrogen oxides and sulphur dioxides, which react with water in rain, clouds and fog, to make acid rain. Aluminium hydroxide (Gibbsite) production accounts for 17 % due to the burning of fossil fuels for heating the dissolution process. The rest is emissions from natural gas production, electricity generation and blasting (rust and corrosion treatment).

The introduction of hydrogen results in a direct reduction of almost 5 %, and the production of hydrogen gas accounts for 8 % of the impact. The majority of this impact can be assigned to various processes contributing to petroleum refineries and hence the steam reforming of hydrogen. This involves fossil fuels, petroleum transport by ship, waste natural gas and blasting, all carbon-based substances producing VOCs and NOx.

The hydrogen fluoride by-product reduces the total impact by 50 %. Sulphuric acid used in the chemical reaction in hydrogen fluoride production accounts for 25 %, while transportation by ship and freight lorry account for one-third. The remaining impacts are associated with heat and electricity generation, blasting, waste natural gas and diesel burning.

The carbon reductant accounts for 12 % of the impact due to emissions in the mining and operation of hard coal. Electricity and cryolite production contributes with less than 10 % due to the usage of fossil fuels like natural gas, heavy oil and hard coal for heating.

4.1.3 Fine particulate matter

Figure 4.4: Comparison of the fine particulate matter formation impacts of the carbon anode system and the expanded hydrogen anode system.
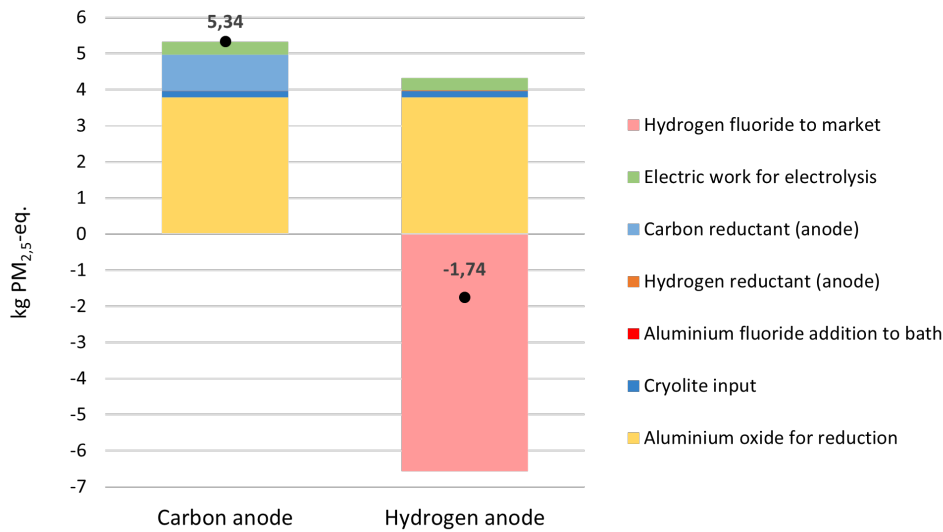
Fine particulate matter is formed from NO_x, NH_3 and SO_2 emitted through the exhaust gas from burning fossil fuels, either directly to the air or by reaction with sunlight and water to form secondary particles. Figure 4.4 displays the contributions to the impact category. As can be seen, the primary contributor is aluminium oxide production which accounts for 70-80 % of both the carbon anode and hydrogen anode system. Heat for the aluminium hydroxide process step and the calcination step contributes 25 % each, and alumina transport by ship accounts for 20 % of this impact. Most alumina is produced in China, Australia, Brazil and India, and the amount not used domestically is shipped to smelters in Canada, Norway, the USA and other countries. Large ships most economically perform this shipping due to the heavy weight and large volumes, consuming large amounts of fossil fuels. Electricity used mainly in coal mining, using brown and hard coal as fuel, accounts for 8 %. Direct dust emissions from bauxite mining and blasting account for the rest.

The introduction of hydrogen to the anode reduces the total impacts by 10 % since the steam reforming of methane gas releases considerably fewer particulates than the prebaked carbon anode production. The carbon reductant production contributes 20 % of the total impacts for the carbon anode system and is caused by the coke and pitch production processes and by the burning of fossil fuels for heating the baking furnace.

The HF by-product reduces the total impact by over 130 %. This is mainly due to the production of sulphuric acid, which emits SO_2 directly due to an incomplete reaction of SO_2 into SO_3 on the catalyst and is performed at high temperatures provided by fossil fuels combustion. The remaining impacts are associated with electricity production and cryolite production.

4.1.4 Freshwater and marine eutrophication

(a) Freshwater eutrophication

(b) Marine eutrophication
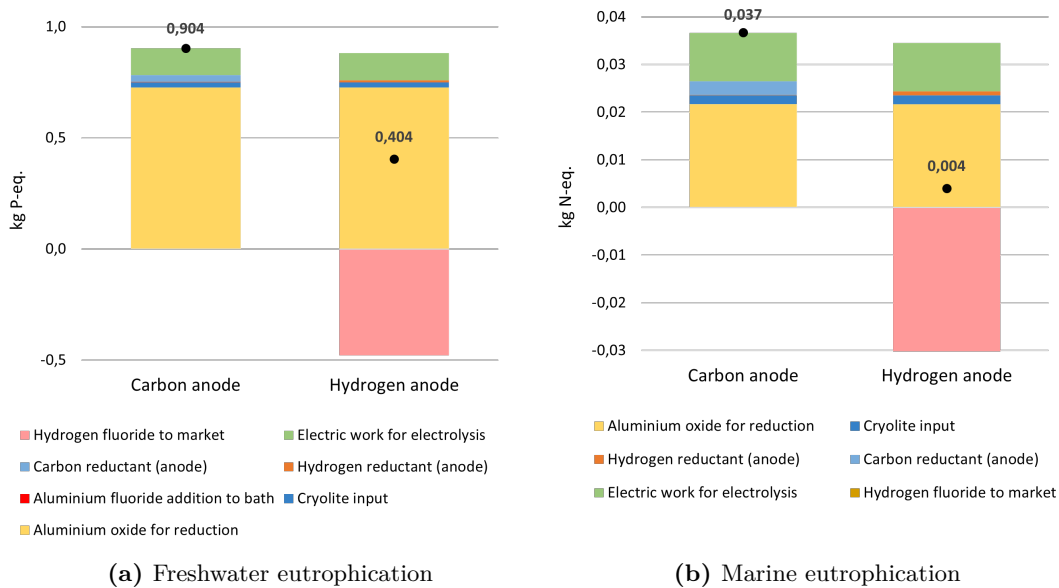
Figure 4.5: Comparisons of the freshwater and marine eutrophication impacts of the carbon anode system and the expanded hydrogen anode system.

As seen from Figure 4.5, the impacts on both freshwater and marine ecosystems are minor compared to the F.U. of 1 t aluminium, but the effect of the hydrogen fluoride by-product is significant.

For the freshwater ecosystem in Figure 4.5a, the aluminium oxide production accounts for 80 % of the impacts, where 75 % is assigned to the red mud digestion into river and groundwater. Phosphorus is tied up in rocks and sedimentary deposits and anthropogenically released through mining operations. 25 % of the impact is a result of coal and copper mining and through nitrogen oxides released from the burning of fossil fuels.

The hydrogen anode reduces the total impact by 2.5 %, while the avoided burdens of the HF by-product reduce the total impact by 55 %. Coal mining contributes over half, and copper mining with over one-third of this impact. Electricity contributes 15 %, where spoils from coal and copper mining account for almost two-thirds and one-third of this contribution, respectively.

For the marine ecosystem in Figure 4.5b, aluminium oxide production accounts for 59 and 63 % of the impacts. Coal mining accounts for 57 %, and sugarcane production has the second highest contribution with 12 %. Sugarcane is a commonly used raw material for biofuel in Brazil, where large amounts of aluminium oxide production occur. The rest of the impact is accounted for by wastewater treatment, uranium in yellowcake used to prepare uranium fuels, and numerous small waste contributions from numerous background processes.

Using a hydrogen diffusion anode reduces the total impacts by 6 %, due to the increased use of natural gas and biofuel as fuel, at the expense of coal and oil. The HF by-product reduces the total impact by almost 90 %, whereas avoided coal mining contributes 55 % and copper mining 12 %. Electricity contributes 30 %, and the contribution is mainly associated with coal and copper mining, the production of biofuel and various wastewater treatments.

4.1.5 Terrestrial acidification and ecotoxicity

(a) Terrestrial acidification   **(b)** Terrestrial ecotoxicity
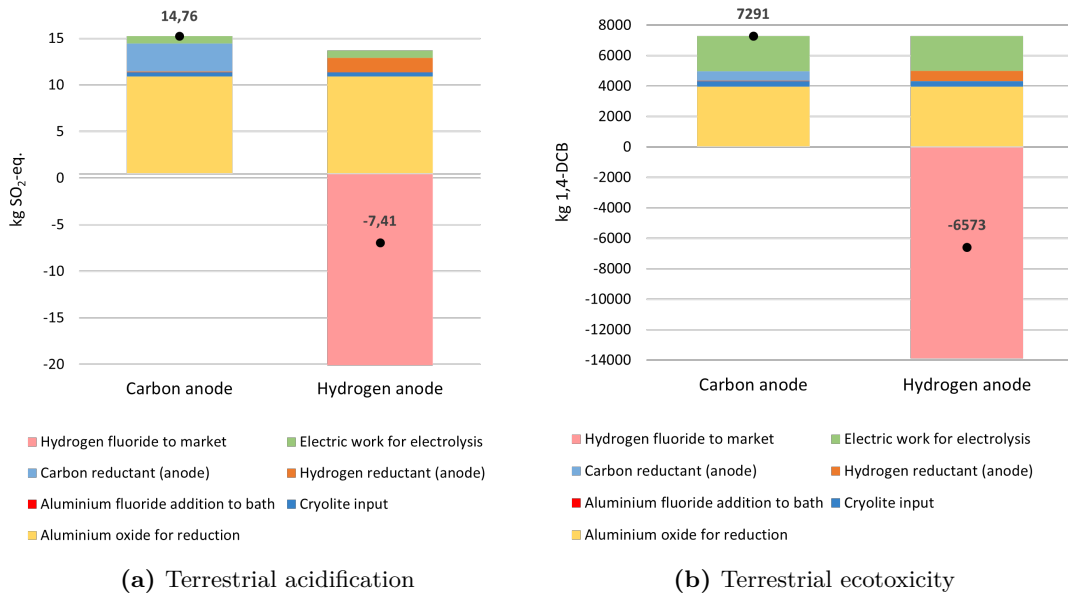
Figure 4.6: Comparisons of the terrestrial acidification and ecotoxicity impacts of the carbon anode system and the expanded hydrogen anode system.

For the terrestrial acidification impacts illustrated in Figure 4.6a, the aluminium oxide production accounts for 70-80 % of the impacts. One-third is associated with burning fossil fuels like natural gas, heavy oil and hard coal for calcination, and 25 % is related to shipping aluminium oxide by ship due to the use of fossil fuel. Burning fossil fuels releases nitrogen oxides and sulphur dioxides, which react with water in rain, clouds and fog to make acid rain. 25 % of the impact comes from the aluminium hydroxide production, the red mud waste from the digestion of bauxite, with nitrogen oxides and sulphur oxides contaminating the groundwater.

The hydrogen diffusion anode reduces the total impact by 10 %, while the HF by-product reduces the total impact by 150 %. Avoided acidification is mainly because of the avoided production of sulphur and sulphuric acid, which contributes to 75 % of the impacts, due to the burning of fossil fuels for heating the sulphuric acid process and the mining process to reach sulphur deposits.

The carbon reductant contributes 20 % to the total impact. Nitrogen oxides (NO_x) and sulphur dioxides (SO_2) from burning heavy oil and natural gas for heating in the production process of the prebaked anode account for 50 %. Petroleum coke and pitch production account for 30 %, and heat and transport account for the rest. The common reason for these emissions is the burning of fossil fuels that contributes to terrestrial acidification, from NO_x and SO_2 emissions.

As seen in Figure 4.6b, the impacts on terrestrial ecotoxicity are substantial, amounting to 7.3 tonnes of 1.4-$DCB_{eq.}$ per tonne liquid aluminium produced. The total impacts are almost identical for the two systems, the hydrogen diffusion anode increases the impacts by 0.3 %. The two main impacts common for the two are aluminium oxide and electricity production, contributing 55 % and one-third, respectively. The aluminium oxide contribution is 43 % heat from the oil and hard coal and 18 % from the air pollutants of copper, nickel and chromium. Of the electricity contribution, 75 % is the production of copper used in transmission and distribution networks due to its high electrical conductivity. Nickel and chromium production account for 10 %, while the rest is assigned to various emissions such as brake wear emissions and process electricity generation.

The avoided burdens from the HF by-product results in a 190 % reduction of the total impacts. The reduction is mainly a result of the avoided copper, zinc, nickel and chromium emissions from mining operations. HF is produced from fluorspar and sulphuric acid, and sulphuric acid is produced from sulphur at 450 °C using a vanadium catalyst. Copper is widely used in electric transport in energy generation, and heat production from fossil fuels releases various toxic substances.

Hydrogen production contributes 10 %, where 90 % is assigned to the direct process by the emissions from vanadium, nickel and copper production. Steam reforming of hydrogen from natural gas at high temperatures uses a nickel catalyst, while copper and vanadium are used in electric transmission and generation equipment. Steam reforming involves balancing the H_2/CO ratio, the water gas shift reaction. It is a multiple-step process occurring at high and low temperatures, where the high-temperature catalyst is iron oxide and chromium oxide, while the low-temperature catalyst is copper-based.

4.1.6   Freshwater and marine ecotoxicity

(a) Freshwater ecotoxicity   **(b)** Marine ecotoxicity
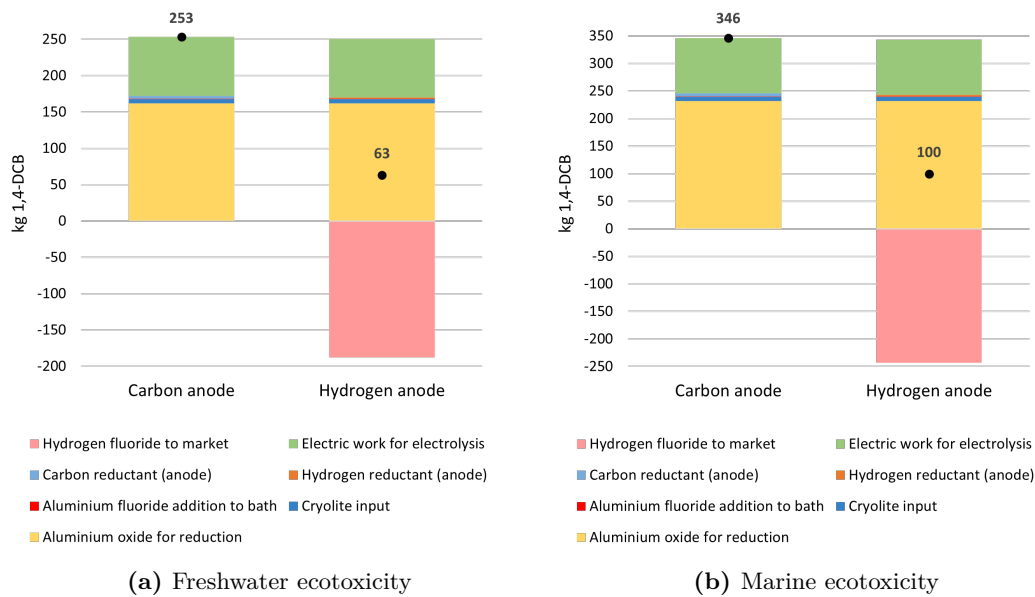
Figure 4.7: Comparisons of the freshwater and marine ecotoxicity impacts of the carbon anode system and the expanded hydrogen anode system.

As seen from Figure 4.7 (on the previous page), the amounts are slightly different, but the distribution of the impacts is almost identical for both categories. Aluminium oxide production accounts for two-thirds, where groundwater and river contamination from the heavy metals in the red mud landfills accounts for 85 %.

Using hydrogen instead of carbon anode reduces the freshwater impact by 1 % but increases the marine impact by 1 %. This is because the natural gas used for producing hydrogen is made at petroleum refineries located off-shore, and 16 % of the marine ecotoxicity impact is assigned to off-shore processes.

The HF by-product results in a reduction of the total impacts by around 75 %. Avoided contamination from copper production accounts for 80 %, while the avoided production of zinc, nickel, gold and silver accounts for 10 %. The rest is accounted for by coal production and the red mud residue.

Electricity production accounts for one-third, where over 90 % are attributed to copper mining operations and the rest from coal mining and nickel slag.

4.1.7 Human carcinogenic and non-carcinogenic toxicity

(a) Human carcinogenic toxicity

(b) Human non-carcinogenic toxicity
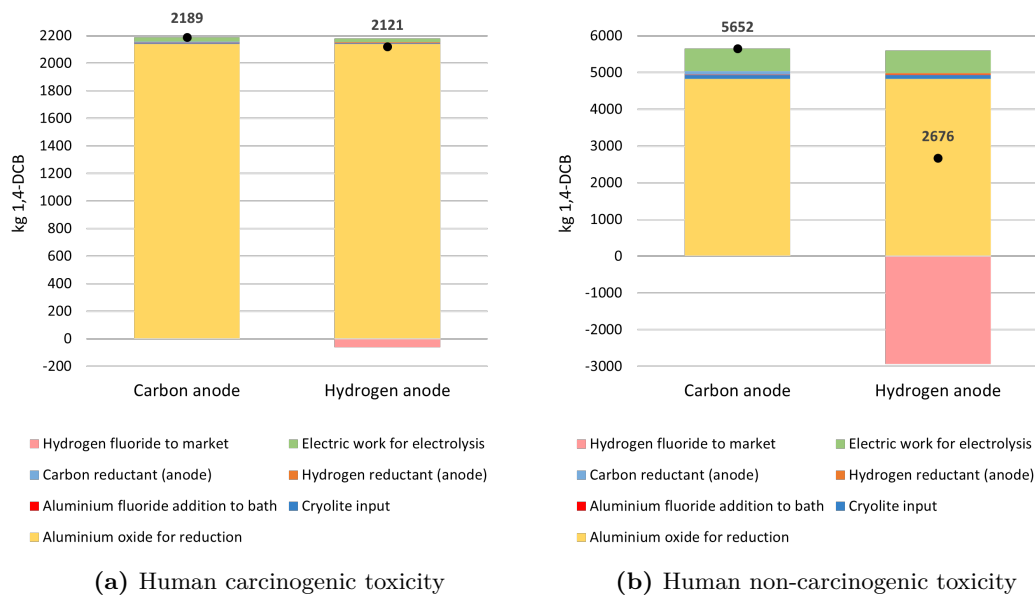
Figure 4.8: Comparisons of the human carcinogenic and non-carcinogenic toxicity impacts of the carbon anode system and the expanded hydrogen anode system.

Regarding carcinogenic toxicity, Figure 4.8a shows that the impact is almost exclusively assigned to the production of aluminium oxide, accounting for 98 % of the total impact. The main reason for the aluminium oxide contribution is the red mud, accounting for 99 %. This slag from the landfills is leached into the soils and groundwater, containing heavy metals such as vanadium, chromium, nickel and mercury. The carbon reductant, electricity and cryolite production contributes to the final 2 % of the total impacts.

Hydrogen at the anode reduces the impact only by 0.3 %, while the avoided burdens from the HF by-product reduce the total impact by 3.1 %. The by-product reduction is a consequence of avoiding slag and dust from producing steel used in the furnace, leaching of spoils in surface landfills from coal mining and slag and sulphidic tailings from copper production.

The non-carcinogenic impacts in Figure 4.8b are also mainly accounted for by the aluminium oxide production, by 85 %, with the red mud as the primary contributor. Hydrogen at the anode reduces the total impacts by 1 % due to high emissions of heavy metals reaching rivers from oil refineries.

As opposed to the carcinogenic impact results, regarding the non-cancer effects, the HF by-product reduces the total impact by 53 %. Slag and sulphidic tailings from copper production account for 65 % of the avoided impact, while spoiling, ash and slurry from coal mining accounts for 12 %. Mining of precious metals such as gold, silver and zinc used in electronics and as catalysts account for 20 %.

Electricity contributes 11 %, where 70 % is copper production and 20 % is coal mining.

4.1.8   Land use
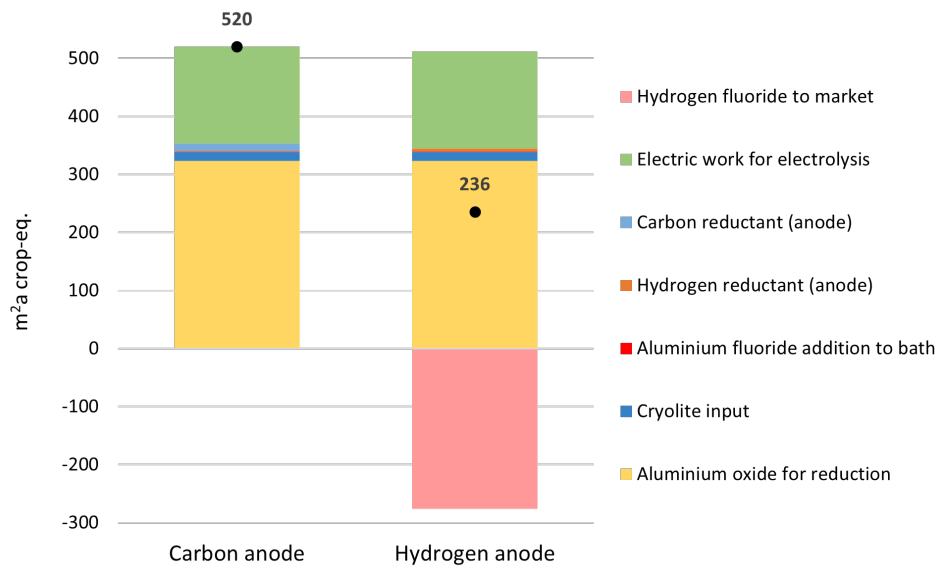
Figure 4.9: Comparison of the land use impacts of the carbon anode system and the expanded hydrogen anode system.

Figure 4.9 shows that aluminium oxide production is the main contributor, accounting for over 60 % of the impacts. Occupation of area for both mining and red mud waste landfills accounts for 90 % of the impact, while the last 10 % is accounted for by road construction, pipelines for natural gas and onshore petroleum infrastructure.

The HF by-product reduces the total impact by 55 %. Avoided occupation of the area for the power plants accounts for over 80 %, while the remaining is associated with forestry and onshore petroleum wells. Electricity contributes one-third, where 80 % is accounted for by the occupation of areas for power plants and the remaining from forestry. The anode materials contribute only 2 % and cryolite with 3 %.

4.1.9 Mineral and fossil resource scarcity

(a) Mineral resource scarcity

(b) Fossil resource scarcity
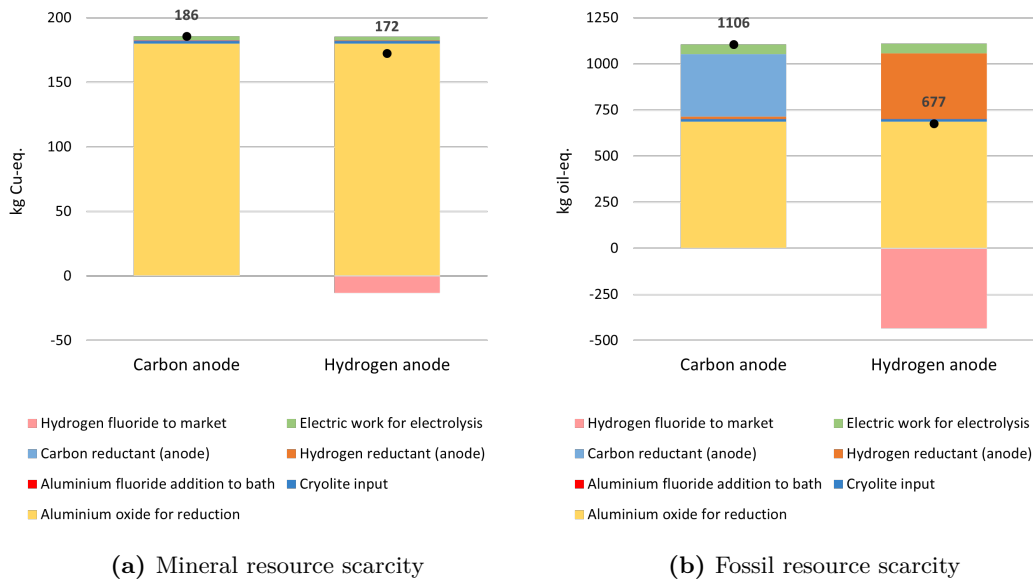
Figure 4.10: Comparisons of the mineral and fossil resource scarcity impacts of the carbon anode system and the expanded hydrogen anode system.

As seen in Figure 4.10a, the mineral resource scarcity is almost exclusively affected by the bauxite mining of the aluminium oxide production, accounting for 97 % of the total impacts. The hydrogen anode only reduces the total impact by 0.2 %, while the HF by-product reduces the total impact by 7.2 %. The contribution from avoided HF production is associated with mining precious metals used as catalysts and in electrical equipment, such as nickel, zinc and copper. The carbon reductant, electricity and cryolite contribute 3 %.

Figure 4.10b illustrates that the contributions affecting fossil resource scarcity are more varied than for the minerals considerations. Aluminium oxide production is still the main contributor, by almost two-thirds, due to the production of fossil fuels, with natural gas and petroleum as the two main sources. The carbon reductant contributes 30 % to the total impact. Petroleum production for the petroleum coke and tar pitch used in the prebaked anode production accounts for over 90 %, while the rest is due to fossil fuels used to heat the anode baking furnace.

The hydrogen diffusion anode increases the total impacts by 0.4 % because hydrogen is produced through steam reforming at petroleum refineries, and the oil refinery uses more fossil resources than coal mining and heating for carbon anode production. The hydrogen production process account for 32 %.

The HF by-product reduces the total impact by 40 %. Natural gas and sulphur production account for two-thirds, while petroleum and coal account for the rest. Fossil fuels provide heat for the combustion of liquid sulphur in the sulphuric acid production to be used in the HF production process and for the rotary kiln in the HF production.

4.1.10 Water consumption
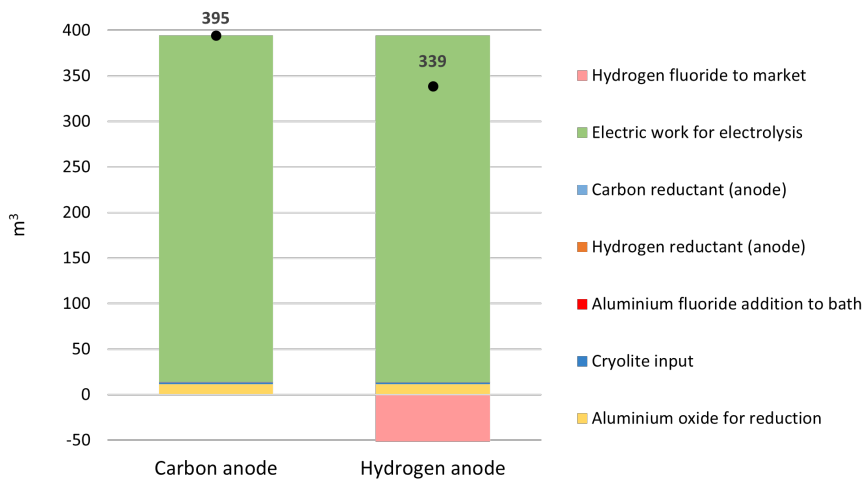
Figure 4.11: Comparisons of the water consumption impacts of the carbon anode system and the expanded hydrogen anode system.

As Figure 4.11 illustrates, in this impact category, aluminium oxide production accounts for only 3 %, while electricity production holds the most significant contribution with 97 %. This is associated with the hydropower reservoir due to the choice of Norwegian electricity production for the modelled aluminium production route.

The carbon and hydrogen production contributes practically nothing, while the HF by-product reduces the total impact by 14 %. This contribution is almost solely assigned to the liquid sulphur used in sulphuric acid production.

4.1.11 Ionizing radiation
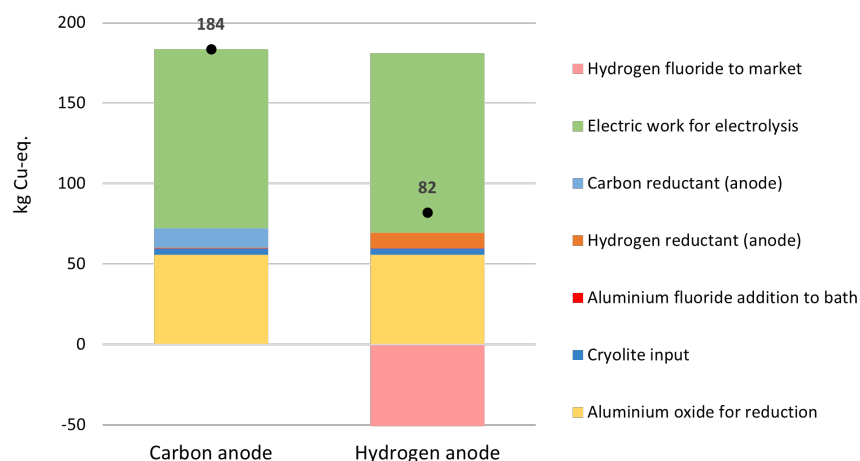
Figure 4.12: Contribution to the Ionizing radiation impact of the carbon anode system and the expanded hydrogen anode system

Figure 4.12 presents the contributions to the ionising radiation impact category, and it shows that the main contributor is electricity production by two-thirds. Uranium tailings account for almost the entire impact and are associated with the imported power mix from Sweden, Finland, Netherlands and Romania, where nuclear power plants are used.

Aluminium oxide production accounts for one-third of the impact and is caused by uranium tailings, the radioactive waste of uranium mining and enrichment, for use in nuclear power plants, mainly from Chinese-made alumina. Hydrogen introduction reduces the total impact by 1.5 %, while the HF by-product reduces the total impact by 55 % due to avoided power consumption from nuclear power plants found in the power mix. The carbon reductant contributes 6 % to the total impact, while cryolite contributes 2 %.

Appendix D provides the characterised and normalised impact results, in Table D.1 and Table D.2, respectively. The normalised results are included to provide a comparison between impact categories, expressed relative to a reference system [78].

4.2   Contribution to endpoint categories

The midpoint results assessed in the previous chapter consist of many impact categories, resulting in a complete and detailed result suitable for identifying important aspects of the product life cycle. The midpoint results can be hard to interpret correctly and be presented clearly and concisely for decision-making purposes. The endpoint results reduce the complexity by presenting the results in three Areas of Protection. The impact results are summarised through normalisation and weighting to provide a compressed and comparable presentation. The averaged weighting factors for the endpoint categories are 40 % for human health and ecosystems, and 20 % for resources, for the hierarchist perspective, and the endpoint results are shown in Figure 4.13.
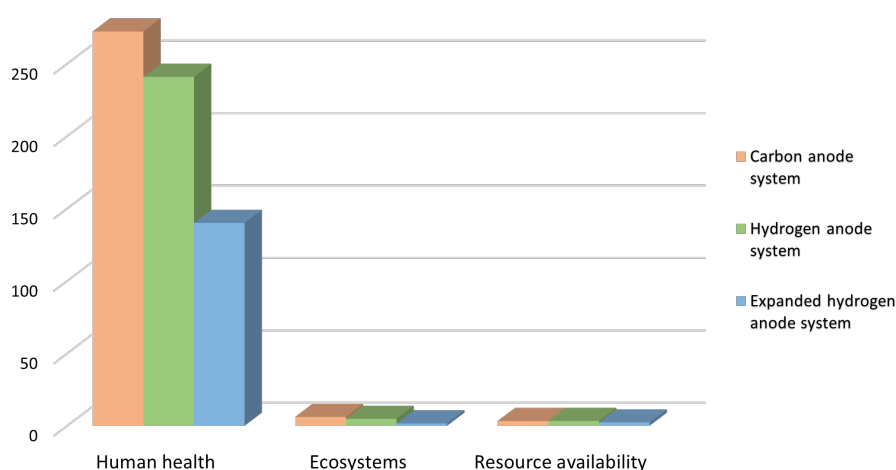
Figure 4.13: Comparison of the weighted endpoint impacts of the carbon anode system, the hydrogen anode system and the expanded hydrogen anode system.

Figure 4.13 shows that aluminium electrolysis affects human health substantially more than the ecosystems and resources. The carbon anode system has a higher impact on human health and ecosystems, while the hydrogen system has a higher contribution associated with the resources. This is in accordance with the midpoint impact results, where the fossil resource scarcity category is more affected by the hydrogen system but by less than 1 %. The expanded hydrogen system has a lower impact in all categories, by the midpoint impacts, where the avoided production of HF further reduced the impacts in all categories compared to hydrogen diffusion anode without system expansion.

By grouping the endpoint impact results as shown in Figure 4.14 below, it is clear that the hydrogen anode has a lower contribution to the overall endpoint impacts.
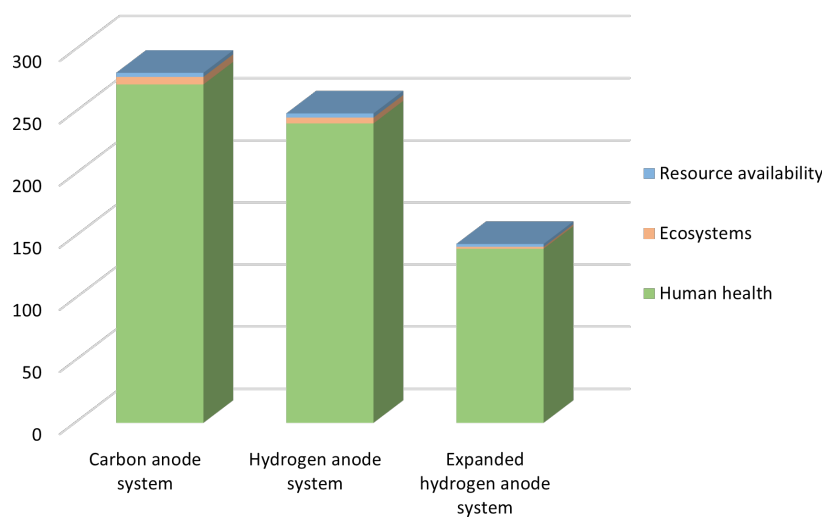
Figure 4.14: Comparison of the endpoint impacts by aggregation

Table D.3 in Appendix D displays the endpoint impact results for the endpoint assessment together with normalised and weighted results.

4.3   Uncertainty and sensitivity analysis

To provide a precise interpretation in compliance with the scope of the study, the results of this LCA must be evaluated with regard to uncertainty and accuracy.

- **Data availability:** In this assessment, the hydrogen diffusion anode approach holds a significant degree of uncertainty, as it is a novel approach at the experimental research stage. Data is obtained from literature and process simulations and provides sufficient accuracy to develop an inventory for small scale based on stoichiometric and partly real condition data. Upscaling these considerations will impose an accumulation of uncertainties caused by energy losses. Further research and experimental data are needed to identify the actual losses in the alternative process.

- **Model assumptions:** When modelling the system of this study, several choices are made. The accuracy of these assumptions could be significant. For example, the conversion rate of hydrogen to HF is assumed from equilibrium calculations, when in reality it is probably lower due to losses. At the same time, there might be secondary reactions in the cell that contributes to the HF generation from hydrogen. The model must be re-evaluated and modified when experimental data are available to obtain more precise results.

- **Data accuracy:** The data Ecoinvent 3.6 is used in this study, updated in 2019, whereas the newest version is compiled in 2023. This causes uncertainty towards the technological advances used in the analysis if some unit processes correspond to years or technology not suitable for the scope of the study. The present study has aspired to use representative data to the best possible extent, to produce correct and robust results, and comply with the Goal and Scope.

- **Scope of the study:** As mentioned, an LCA is highly case-dependent and is subjective modelling, where numerous choices are made throughout the development of the study. The uncertainty lies in how changes in conditions affect the environmental impacts. For example, geographical limits could affect the impacts of electricity or heat production. A sensitivity analysis is used to investigate the system's robustness regarding changes in conditions for the production process.

4.3.1 Uncertainty of the results

The numerous minor uncertainties accumulated from the limitations of available data, model assumptions, data accuracy and scope of the study, result in more considerable uncertainty for the final impact results. The iterative nature of an LCA provides the possibility to re-evaluate the choices made and modify the models of primary aluminium production routes, to improve the comparative assessment.

In this study, the data available for the conventional production route is more precise and comprehensive than that of the alternative production route. For the consumable carbon anode system, both independent and industry-provided LCAs and statistics are available. The electrolysis cell is still a somewhat complex process when modelling chemical reactions. Numerous intermediate and side reactions are occurring, facilitating phase changes and other reactions. For this study, the chemistry is simplified for the model to consist of only the reactions affecting the anode reaction and hydrogen fluoride evolution. The data regarding hydrogen diffusion anode is scarce, and for example, assumptions regarding reaction rates have been chosen based on literature and equilibrium considerations. Considering the above considerations, the hydrogen diffusion anode system impact is more sensitive to change in a future LCA.

4.3.2 Sensitivity to electricity mix

This LCA has been performed for Norwegian production conditions, subsequently, European conditions. The energy crisis during the last year has accelerated the energy trading cooperation across Europe [82]. That scenario will further increase due to increased energy demand to reach the Paris Agreement goal and provide a stable

energy supply security across Europe [82]. A sensitivity analysis is carried out to assess how the primary aluminium production process relies on the electricity source. The Norwegian electricity mix relies heavily on hydropower and wind power, by 88 % and 11 %, respectively [83]. In contrast, 40 % fossil fuels cover the European mix, 25 % nuclear power and one-third of renewable sources [84]. Aluminium smelters are usually located in areas with access to large amounts of cheap electricity, which can result in a different power mix from the general electricity mix. This is not an issue for Norwegian aluminium smelters since almost the entire mix is renewable. It affects the European mix more because the industrial mix has a larger share of hydropower and nuclear power than the general mix. So in this analysis, the Norwegian electricity mix is substituted with the "Electricity, high voltage, aluminium industry IAI Area, EU27 & EFTA | market for | APOS, U".

The impact results of this substitution are shown in Figure 4.15.
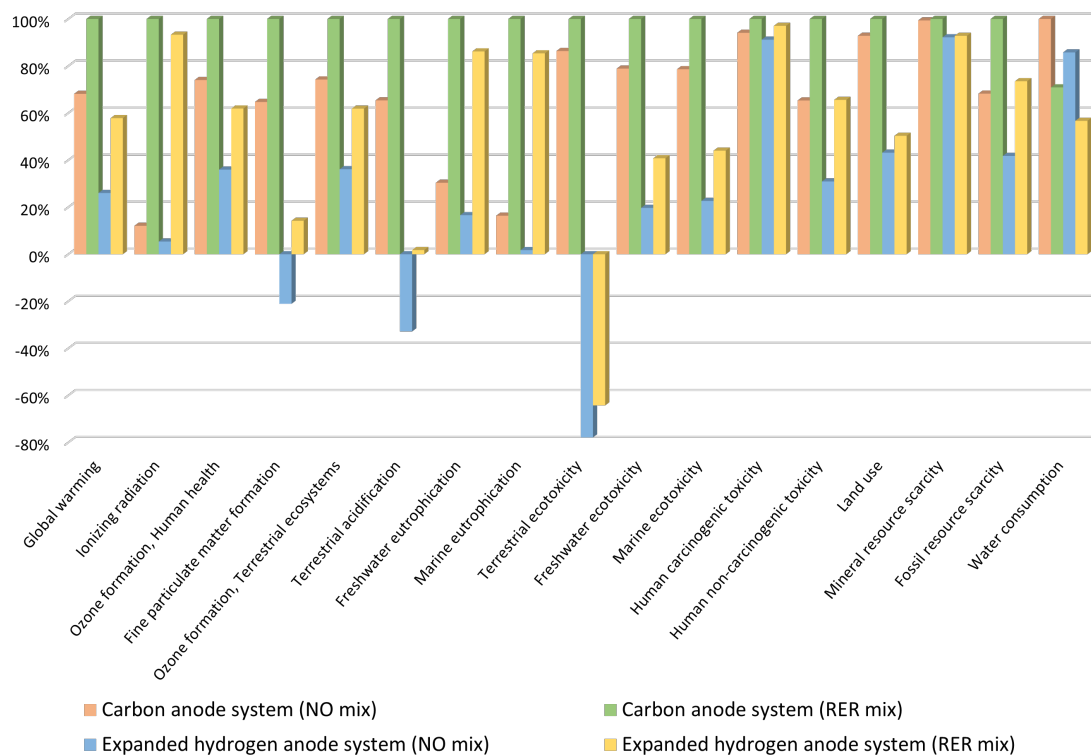
Figure 4.15: Impact results using European electricity mix in the electrolysis process. Comparison of the midpoint impact results of the carbon anode system and the expanded hydrogen anode system with Norwegian and European electricity mix.

The European electricity mix increases impacts in all categories for both the carbon anode and the expanded hydrogen anode system. The increased impacts are very noticeable in the impact categories where the burning of fossil fuels is the main contributor, such as global warming, ozone formation, fine particulate matter formation and acid-

ification. Nuclear power and coal are responsible for the most significant increases, in the ionising radiation and eutrophication impacts, respectively.

Marine resource scarcity and human carcinogenic toxicity are the least dependent on the electricity source because nearly the entire impact is caused by bauxite mining operations and red mud residue from the Bayer process.

Norwegian smelters have a significant advantage connected to geographical boundaries since they use hydropower for the energy-intensive primary aluminium production process. The impact difference is identical for the two production routes, since the modelled electricity is the electrolysis requirement, and is the same for both production routes. The hydrogen diffusion anode production route is favoured independently of the change in the electricity mix.

The detailed results of the sensitivity to electricity mix are provided in Table E.1 in Appendix E.

4.3.3 Sensitivity to hydrogen production method

As mentioned in Chapter 1.3, hydrogen could be produced by several methods. The future alternative is green hydrogen, produced by water electrolysis, using renewable energy sources for electricity. This sensitivity analysis modifies green hydrogen production with renewable electricity and water as inputs. The electricity needed to produce 1 kg of hydrogen is ideally 39 kWh [59]. Most commercial electrolysers have efficiencies between 56 % and 73 %, corresponding to electricity consumption between 53.4 kWh and 70.1 kWh per kg hydrogen [85].

The average electricity requirement of 62 kWh, and 8.9 litres of water per kg hydrogen [59] is used to calculate the 6.9 MWh electricity and 1 m_3 of water input. The material requirements for the electrolyser and infrastructure are not considered, which results in underestimating the impacts. The simplified modelling of zero-emission hydrogen production still provides a useful estimate of the effects of changing from grey to green hydrogen. The Norwegian electricity mix in ecoinvent is manually modified to consist of hydropower and onshore wind power without power import [83, 86]. The results are shown in Figure 4.16.
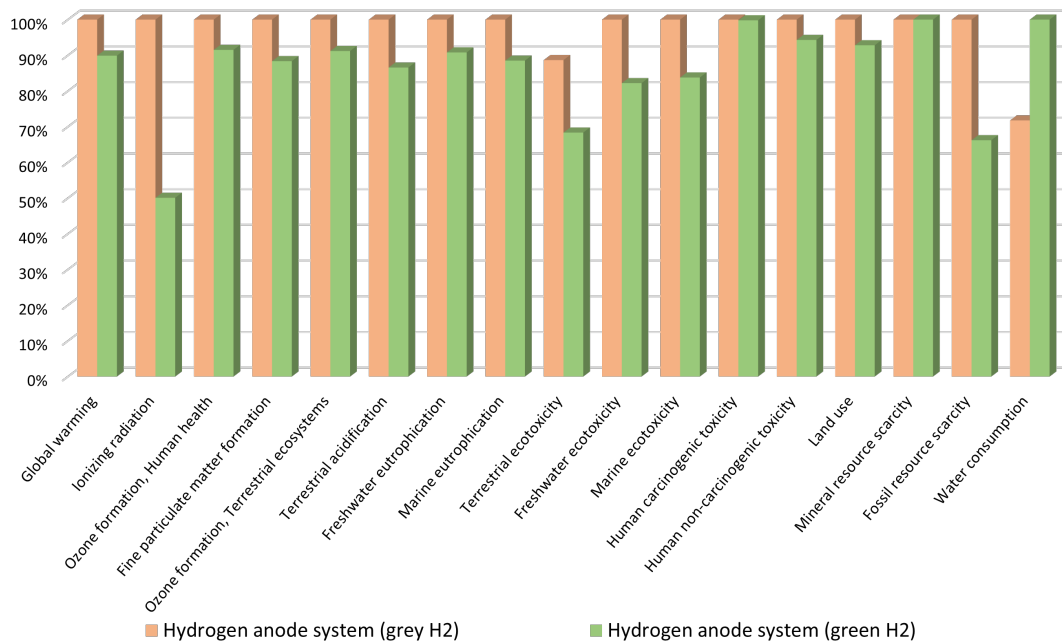
Figure 4.16: Comparison of the impact results for hydrogen production by steam reforming and electrolysis using renewable energy sources for the hydrogen diffusion anode system.

The results in Figure 4.16 represent the hydrogen diffusion anode system, without HF as a by-product. The two approaches need the same amount of hydrogen, meaning the changed impacts are the same, only the percentage difference varies slightly. The overall result is the same for both systems, that is the green hydrogen reduces the impact in all categories except water consumption. The environmental impacts are significantly reduced in the ionising radiation, terrestrial ecotoxicity and fossil resource scarcity impact categories. This is associated with the avoided nuclear power and fossil fuel consumption in the electricity mix. For terrestrial ecotoxicity, the reduction is caused by the reduced requirements for copper used in power generators.

Half the categories experience between 7 % and 18 % lower impacts. The high share of hydropower in the modelled electricity mix increases water consumption but reduces the use of copper and precious metals for power generation equipment. The equipment used in a hydropower plant has a long lifetime and needs few components to produce power, such as pipes and turbines. This could have been different if solar or wind power plants were exclusively used, with increased demand for minerals, precious metals and aluminium. E.g., if only wind power is used, the terrestrial ecotoxicity impact increase by over 300 % due to the copper used in the power generators in the turbine.

Compared to the original production method using a carbon anode, the GHG emissions are reduced by 45 %, a further reduction of 7 % compared to grey hydrogen.

Detailed results of the sensitivity analysis regarding the hydrogen production method, including the wind power alternative, are presented in Table E.2 in Appendix E.

4.3.4 Sensitivity to fuel source in HF production

As mentioned in Chapter 1.3, the conventional production process of hydrogen fluoride is the reaction between fluorspar and sulphuric acid (H_2SO_4) in a rotary kiln furnace. The heat source is modelled using natural gas in the ecoinvent LCI database. Natural gas is widely used for its ability to produce high temperatures, while alternative fuels might not be suitable due to lower calorific values and hence lower temperatures [87]. Studies on alternative fuel sources for rotary kilns used in cement manufacturing showed that the use of high and low calorific value fuels simultaneously as possible, with replacement rates of 40 % to 100 % [88, 89], where the studied fuel sources included dry sewage sludge, carpet residues, biomass and waste oil [88, 90].

With further research and experimental studies to avoid harmful effects on the product quality, a flexible multi-fuel furnace is a possible future solution [90]. The ratio of 50 % natural gas and 50 % biomass is used in the model used for this sensitivity analysis from the satisfactory results by the use of 55 % alter[89]. Biomass is chosen because it is a renewable energy source, given that only the annual growth of the biomass source is utilised, and 5 % of the Norwegian power production is made from biomass, potentially doubling this production [91].

To model the change, the HF production process is the only process which has been changed. The "Hydrogen fluoride RER| market for hydrogen fluoride | APOS, U" has been affected in the production process, where the original heat from "Heat, district or industrial, natural gas RER| market group for | APOS, U" is reduced to 3.5 MJ. The remaining 3.5 MJ is provided by "Heat, district or industrial, other than natural gas DE| heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | APOS, U". The results of the sensitivity analysis regarding the thermal energy source for the furnace in the hydrogen fluoride production process is shown in Figure 4.17.
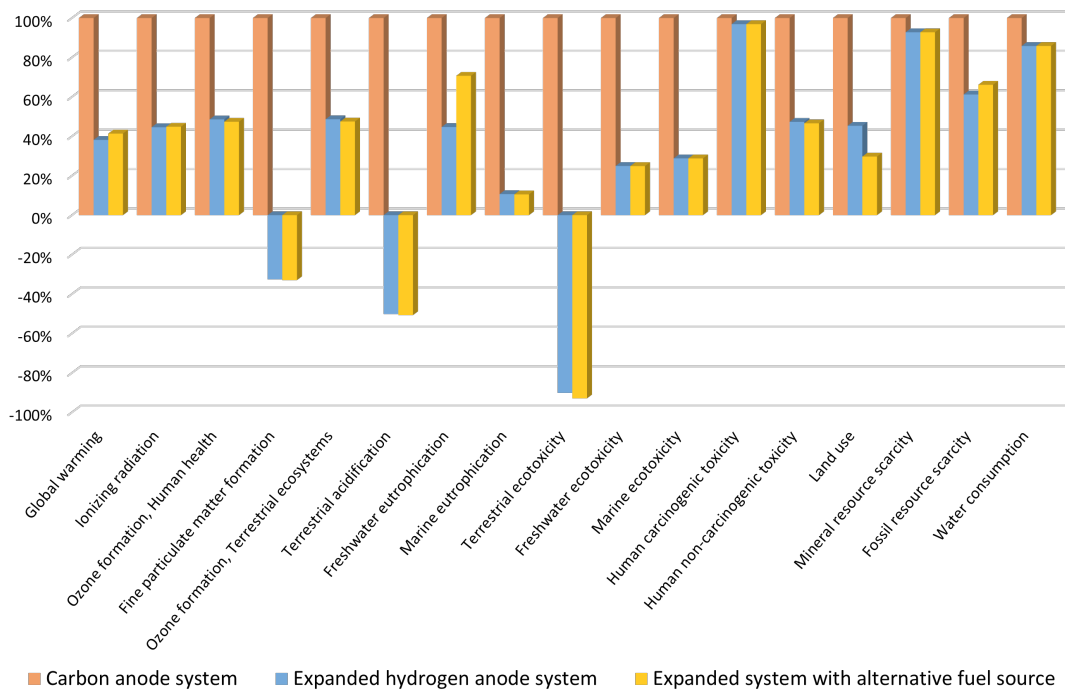
Figure 4.17: Impact results using 50 % biomass and 50 % natural gas for heating the furnace in the hydrogen fluoride production process. Comparison of the midpoint impact results of the carbon anode system, the expanded hydrogen anode system and the expanded system with alternative fuels for HF production.

The overall result is that the introduction of biomass affects the impacts very little. Biomass is said to be renewable if the planting and growing of new trees replenish the used amount. The wood emits GHG emissions but is considered neutral because the planted trees consume CO_2, but this is not shown in the impact results. Freshwater eutrophication experienced increased impact, due to ammonia produced from natural gas, used as a redox mediator to facilitate energy transfer to biomass in the production process.

Detailed results of the sensitivity analysis regarding fuel source for HF production are presented in Table E.3 in Appendix E.

4.3.5 Sensitivity to energy source in aluminium oxide production

The energy sources used in aluminium oxide production vary geographically, where coal, oil, gas and electricity are used at an industrial scale [92]. Australia is one of the largest manufacturers of aluminium oxide, and the production facilities have combined heat and power generation using natural gas, coal, or biomass [93]. There are several ongoing pilot projects regarding alternative fuels for the digestion and calcination process of the Bayer process, where both electrical boilers and electrification are piloted.

Around 70 % of the fossil fuels consumed in the refining process is used to produce steam in boilers, and Alcoa in Australia runs a pilot to demonstrate technology that can electrify the production of steam in its alumina refining process [93]. European countries are responsible for approximately one-quarter of global aluminium oxide export [94]. This sensitivity analysis will substitute the fossil fuels used in the boilers with electricity from wind and solar power. These two are chosen to simulate the future of European renewables since wind and solar power shares of the European electricity mix are increasing [95, 96]. The results are shown in Figure 4.18.
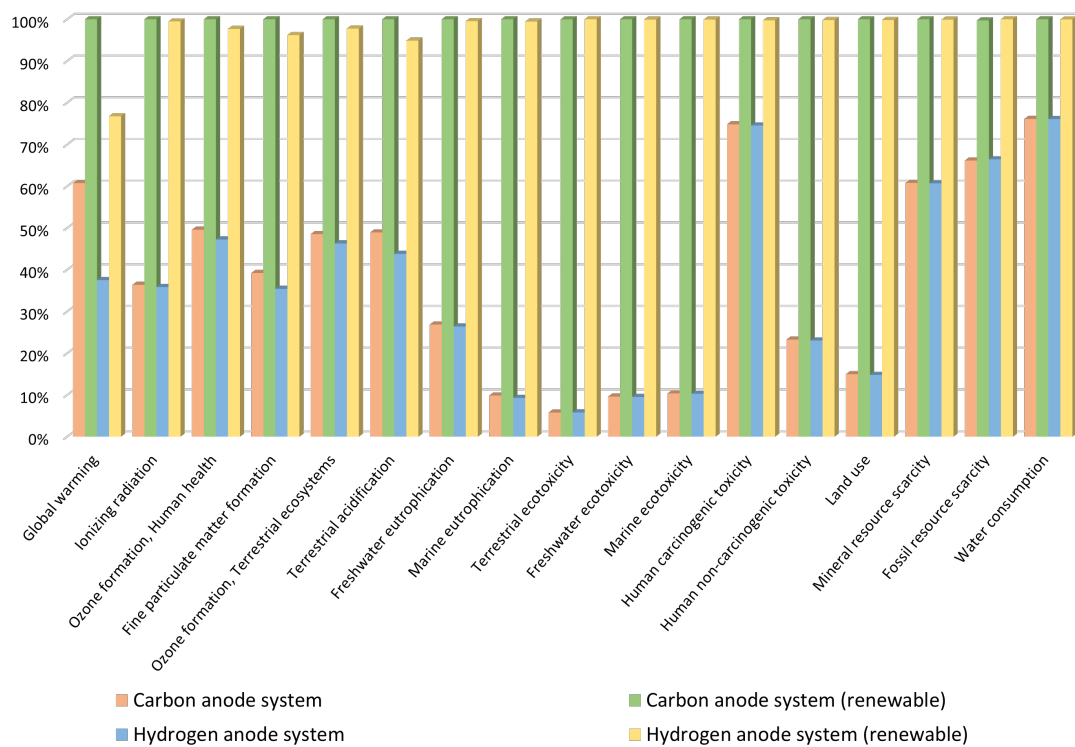
Figure 4.18: Impact results using wind and solar power as energy sources for the aluminium oxide production process.

The result of using wind and solar power to produce aluminium oxide is a remarkable increase in all categories. This is associated with the massive amount of materials required to construct wind turbines and solar panels. The construction of a wind turbine requires more than 100 t steel, 300 t concrete and 2 t copper per MW [97]. For solar power plants, more than 65 t steel, 60 t concrete and 4 t copper are required per MW [97]. Hence, all impact categories associated with mining and resources skyrocket. Fuel sources to provide heat and electricity in the production routes of wind and solar power plants contribute to significant environmental impacts.

Detailed results of the sensitivity analysis regarding energy source for the aluminium oxide production are presented in Table E.4 in Appendix E.

Chapter 5

Conclusion

The research questions from the scope are clearly stated in the conclusion below to provide a clear picture of the assessment and the conclusions made.

What are the life cycle characteristics of the primary aluminium production, using consumable carbon anode and hydrogen diffusing anode, in Norway, and the different impact contributions from the two alternative production routes?

Throughout this research, a life cycle assessment has been made to study the sustainability of the primary aluminium production process using both a conventional carbon anode and an alternative hydrogen diffusion anode. Raw material data has been obtained, a process simulation model has been performed, and the resulting data has been analysed in the LCA software tool SimaPro.

The results show reduced impacts in the hydrogen diffusion anode production route for most of the studied impact categories, and the most significant reduction was experienced in global warming, ionising radiation, ozone formation, fine particulate matter formation, terrestrial acidification, freshwater and marine eutrophication. Nearly half of the impact categories experienced less than one % change, i.e. freshwater and marine ecotoxicity, human carcinogenic and non-carcinogenic toxicity, mineral and fossil resource scarcity and water consumption. Terrestrial ecotoxicity and fossil resource scarcity experienced an increase in impact when using a hydrogen diffusion anode.

The fuel sources for heat in hydrogen production explain the small to moderate reductions in many impact categories. While the fossil fuels and carbon used for prebaked anode production are avoided, most hydrogen produced today is made from methane steam reforming. Hence, the impacts are similar in many categories, but the contributing fossil fuel sources and unit processes change. The main direct effect of changing from carbon anode to hydrogen anode is the reduced direct process emission from the consumed carbon anode, reducing the global warming impact by 38 %.

A system expansion by substitution was performed on the hydrogen diffusion anode system, to include the hydrogen fluoride waste emission as a by-product for internal recycling or use in the HF market. The result was a significant reduction in all impact categories.

For both the conventional carbon anode system and the hydrogen diffusion anode system, the refining of aluminium oxide accounts for between 55 % and 98 % of the impacts in 13 of 15 categories. Burning fossil fuel for electricity and heat in the digestion and calcination processes is responsible for between 50 % and 80 % of the impacts in global warming, ozone formation, fine particulate matter formation, terrestrial acidification and fossil resource scarcity categories. The red mud waste from the Bayer process accounts for between two-thirds and 98 % of the impacts in the freshwater and marine ecotoxicity, human carcinogenic and non-carcinogenic toxicity and freshwater eutrophication categories. The mining of bauxite accounts for 60 % and 97 % of the land use and mineral resource scarcity impact categories, respectively. Coal mining and biofuel production account for 60 % of marine eutrophication.

The reason for the reduction in most of the impact categories being small is as mentioned, that 90 % of the hydrogen produced today is produced by methane steam reforming, reducing impacts slightly because natural gas emits less than petroleum for the prebaked anode production.

The main effect of using hydrogen instead of carbon at the anode is reduced global warming impact by 38 % and a 10 % reduction in fine particulate matter formation and terrestrial acidification.

The significant reduction in this research is experienced when the hydrogen system is expanded to include the hydrogen fluoride emission as a by-product. The HF can be recycled internally and reused in the bath or used in the refrigerant industry. The system expansion results in a reduction between 55 % and 190 % in 11 of 15 impact categories. These substantial reductions are strongly linked with the avoided consumption of fossil fuels for heating the furnace in the production of HF and sulphuric acid. The second hotspot for the expanded system is the avoided impacts from mining and production of copper and precious metals used as catalysts and power transmission and generation.

The endpoint impact assessment showed that the human health and ecosystems categories have lower impacts for the hydrogen diffusion anode, while the resource availability has a higher impact. This is in accordance with the midpoint results, where the hydrogen anode system has higher impacts in the fossil resource scarcity and terrestrial ecotoxicity categories. The endpoint of resources is grouped only by the two resource scarcity midpoint categories, while the ecosystems endpoint consists of 9 midpoint categories. Hence, the relative contribution to the endpoint category is more significant for fossil resource scarcity than terrestrial ecotoxicity on the ecosystems endpoint.

The aggregated endpoint results clearly show that the hydrogen diffusion anode performs better than the carbon anode system, with an 11 % reduction directly from the change to hydrogen, and by 49 % when including HF as a by-product.

How sensitive is the environmental impact of aluminium production to fuel sources, reductant production method and changes in the electricity mix?

The first sensitivity analysis studied the production systems' sensitivity towards different electricity sources for electrolysis. This will give insight into the production routes for European smelters and for Norwegian smelters experiencing increased European influence on the Norwegian mix. The production process is highly energy-intensive and is highly sensitive to changes in electricity sources, and all impact categories experienced increased environmental impacts. The energy requirements for the chemical reactions using carbon and hydrogen are almost identical, and hence the change in the electricity mix does not change the preferred production route. Proposed further work will be to produce a more comprehensive energy balance and change the electricity source for multiple background flows, to obtain a more robust model.

The second sensitivity analysis investigated how the change in the hydrogen production method would affect the environmental performance of the aluminium production route. Grey hydrogen from methane steam reforming was changed to green hydrogen from water electrolysis with renewable energy sources. The result showed a lower impact in almost every category, due to avoided nuclear and fossil fuel production, and reduced demand for copper and other metals.

A key finding of the sensitivity analysis was that the hydrogen production method is highly sensitive to the choice of renewable energy source used in the electrolysis. A quick assessment was performed to highlight this, showing that the exclusive use of wind power for the hydrogen production plants resulted in a 300 % increase in terrestrial ecotoxicity impact due to the extensive amounts of copper used in the turbine generator. It experienced slightly increased GHG emissions, associated with the construction of the turbines, such as cement for the base, fibreglass for the tower and blades and steel. Hydropower uses fewer minerals and metals but occupies large areas and causes significant nature interventions when constructed.

The third sensitivity analysis investigated the fuel source for hydrogen fluoride production, substituting 50 % of the heat from natural gas with heat from biomass. The environmental performance did not change, mostly due to the direct emissions from burning wood and the ammonia from natural gas used in biomass production. The use of biomass could reduce the impacts if produced sustainably, but this is not shown in the results.

The last sensitivity analysis was performed to assess how the main contributing unit process would respond to a change in energy source, namely the aluminium oxide production. Fossil fuels for heat and electricity were substituted with wind and solar power. This resulted in a tremendous overall impact increase, due to the massive material requirements for construction of the wind and solar power plants. Energy sources and raw material extraction in the production of wind turbines and solar panels hold a significant impact on the environmental impacts of renewable energy production.

Final conclusive remarks

In this study, an alternative anode has been proposed for primary aluminium production. The hydrogen diffusion anode shows positive environmental results for a Norwegian aluminium smelter cell. A reduction in almost every impact category resulted from substituting the consumable carbon anode with a hydrogen diffusion anode.

The demand for aluminium in the future will undoubtedly increase, as it is an essential material for the energy transition and the corresponding increased demand for digitalisation and electricity transmission. The production process is highly developed in some regards but has considerable potential for improvement in others, such as in electricity supply and direct process emissions. The consumable carbon anode is the source of 1.5 kg CO_2 per kg liquid aluminium and modifying the anode could contribute to the zero-emission required to retard global warming.

The hydrogen diffusion anode system was expanded to include the hydrogen fluoride emissions as a by-product, for reuse in the bath or fertiliser industry. This resulted in the system performing even better environmentally, primarily associated with avoiding burning fossil fuels and mining.

The hydrogen fluoride emissions contribute less to the environmental impacts than predicted beforehand. The main issue with HF gas concerns the work environment in the production facility, as the gas affects the respiratory system and can cause lung diseases. The research to further improve dry scrubbers and avoid local emissions when the bath is exposed to aluminium oxide during feeding would contribute to minimising this potential hazard.

Further experimental research to obtain more precise data will reduce the uncertainty of the LCA on primary aluminium production by using a hydrogen diffusion anode. This is a novel approach with limited experimental studies, which this master's thesis has aimed to provide a first environmental evaluation of. The uncertainties of the LCA are associated with the practical conditions regarding the large-scale implementation of an approach barely tested experimentally. This thesis still provides a valuable assessment of the alternative aluminium production route, showing that the hydrogen diffusion anode performs better environmentally if implemented in industrial smelter cells.

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Appendix A

Chemical reactions in the electrochemical process

Electrolyte considerations

Cryolite completely ionizes to form hexafluoroaluminate (AlF_6^{3-}) anions, which further dissociates to form tetrafluoroaluminate (AlF_4^-) as well as sodium (Na) and fluoride (F) ions according to Equations (A.1) and (A.2) [25]:

$$Na_3AlF_6 \text{ (s)} = 3\,Na^+ + AlF_6^{3-} \tag{A.1}$$
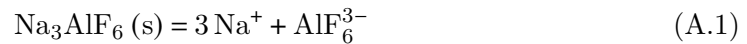
The hexafluoroaluminate ion then dissociates partly as a consequence of the melting process [25]:

$$AlF_6^{3-} = AlF_4^- + 2\,F^- \tag{A.2}$$

The aluminimum fluoride added in excess reacts with F^- ions according to Equation (A.3) [25]:

$$AlF_3 + F^- = AlF_4^- \tag{A.3}$$

Sodium uptake in a cells early life

The uptake of sodium (Na) in the cathode follows the reactions in Equations (A.4) and (A.5) [26]:

$$4\,Na_3AlF_6 + 3\,C_{(anode)} + Al_2O_3 + 6\,x\,C_{(cath)} \rightarrow 6\,NaAlF_4 + 3\,CO_2 + 6\,NaC_x \tag{A.4}$$

$$3\,Na_2CO_3 + 6\,NaAlF_4 \rightarrow 4\,Na_3AlF_6 + Al_2O_3 + 3\,CO_2 \tag{A.5}$$
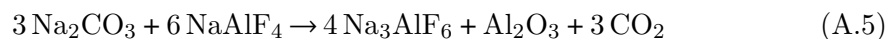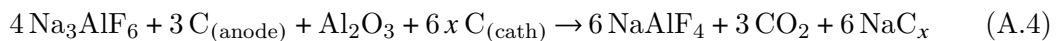
Appendix B

Chemical reactions used in HSC

As described in Chapter 1.3, there are numerous different chemical reactions occurring in the cell. Below are the 7 reactions used in the mass and energy balance in HSC Chemistry.

Overall reactions with carbon and hydrogen anode:

$$\frac{1}{2}\,Al_2O_3\,(s) + \frac{3}{4}\,C\,(s) = Al\,(l) + \frac{3}{4}\,CO_2\,(g) \qquad \text{(1.1 revisited)}$$

$$\frac{1}{2}\,Al_2O_3\,(s) + \frac{3}{2}\,H_2\,(g) = Al\,(l) + \frac{3}{2}\,H_2O\,(g) \qquad \text{(1.11 revisited)}$$
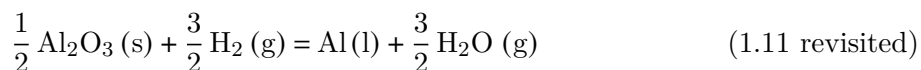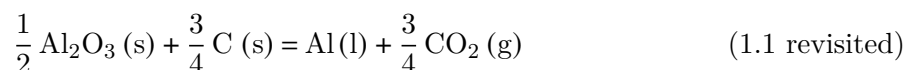
The HF emission reactions used are:

$$2\,Na_3AlF_6\,(l) + 3\,H_2\,(g) = 2\,Al\,(l) + 6\,NaF\,(l) + 6\,HF\,(g) \qquad \text{(1.14 revisited)}$$

$$2\,AlF_3\,(diss) + 3\,H_2\,(g) = 2\,Al\,(l) + 6\,HF\,(g) \qquad \text{(1.15 revisited)}$$

$$2\,AlF_3\,(g\,or\,diss) + 3\,H_2O\,(g\,or\,diss) = Al_2O_3\,(s\,or\,diss) + 6\,HF\,(g) \qquad \text{(1.16 revisited)}$$
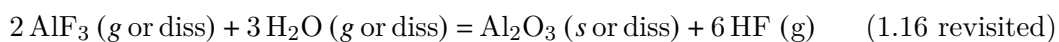
The electrolyte reactions considered are:

$$Na_3AlF_6\,(diss) + 2\,AlF_3\,(diss) = 3\,NaAlF_4\,(g)$$

$$3\,NaAlF_4\,(g) + 3\,H_2O\,(g) = Al_2O_3\,(s) + Na_3AlF_6\,(l,s) + 6\,HF\,(g) \qquad \text{(1.17 revisited)}$$
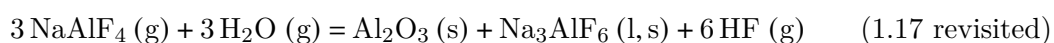
Appendix C

Inventory

Table C.1: Inventory for the electrolysis with carbon anode in SimaPro per F.U.

Input/output	Amount	Reference
Outputs to technosphere: Products		
Liquid aluminium	1 t	System F.U.
Inputs from technosphere: Materials/fuels		
Aluminium oxide, metallurgical IAI Area, EU27 & EFTA | market for aluminium oxide, metallurgical | APOS, U	1.889 t	[10]
Cryolite GLO | market for | APOS, U	0.018 t	[30]
Aluminium fluoride GLO | market for | APOS, U	0.002 t	[30]
Anode, prebake, for aluminium electrolysis IAI Area, EU27 & EFTA| anode production, prebake, for aluminium electrolysis | APOS, U	0.425 t	[14]
Hydrogen, gaseous GLO | market for hydrogen, gaseous | APOS, U	0.004 t	[53]
Inputs from technosphere: Electricity/heat		
Electricity, medium voltage NO | market for | APOS, U	13 MWh	[18]
Emissions to air		
Carbon dioxide	1.56 t	[16]
Hydrogen fluoride	0.018 t	Mass balance HSC

Table C.2: Inventory for the electrolysis process with hydrogen diffusing anode in SimaPro per F.U.

Input/output	Amount	Reference
Outputs to technosphere: Products and co-products		
Liquid Al	1 t	F.U. of the system
Outputs to technosphere: Avoided products		
Hydrogen fluoride RER | market for hydrogen fluoride | APOS, U	0.80 t	Mass balance HSC
Inputs from technosphere: Materials/fuels		
Aluminium oxide, metallurgical IAI Area, EU27 & EFTA | market for aluminium oxide, metallurgical | APOS, U	1.889 t	[10]
Cryolite GLO | market for | APOS, U	0.018 t	[30]
Aluminium fluoride GLO | market for | APOS, U	0.002 t	[30]
Hydrogen, gaseous GLO | market for hydrogen, gaseous | APOS, U	0.112 t	Stoichiometric
Inputs from technosphere: Electricity/heat		
Electricity, medium voltage NO | market for | APOS, U	13 MWh	[18]

Appendix D

LCIA results

Table D.1: Characterization results of the Life Cycle Impact Assessment (F.U. of 1 t liquid Al in Norway).

Impact category	Units	Carbon anode	Hydrogen anode	Expanded system
Global warming	kg CO$_{2eq.}$	4 273	2 638	1 632
Ionizing radiation	kBq Co-60$_{eq.}$	184	181	82
Ozone formation, human health	kg NOx$_{eq.}$	8.4	8.0	4.1
Fine particulate matter formation	kg PM$_{2.5eq.}$	5.3	4.8	-1.7
Ozone formation, terrestrial eco	kg NOx$_{eq.}$	8.5	8.1	4.1
Terrestrial acidification	kg SO$_{2eq.}$	14.8	13.2	-7.4
Freshwater eutrophication	kg P$_{eq.}$	0.904	0.882	0.404
Marine eutrophication	kg N$_{eq.}$	0.037	0.035	0.004
Terrestrial ecotoxicity	kg 1.4-DCB$_{eq.}$	7 291	7 313	-6 573
Freshwater ecotoxicity	kg 1.4-DCB$_{eq.}$	253	251	63
Marine ecotoxicity	kg 1.4-DCB$_{eq.}$	346	343	100
Human toxicity (carcinogenic)	kg 1.4-DCB$_{eq.}$	2 189	2 181	2 121
Human toxicity (non-carcinogenic)	kg 1.4-DCB$_{eq.}$	5 652	5 602	2 676
Land use	m^{2}a crop$_{eq.}$	520	512	236
Mineral resource scarcity	kg Cu$_{eq.}$	186	186	172
Fossil resource scarcity	kg oil$_{eq.}$	1 106	1 110	677
Water consumption	m^3	395	394	339

Table D.2: Normalised results of the Life Cycle Impact Assessment (F.U. of 1 t liquid Al in Norway)

Impact category	Units	Carbon anode	Hydrogen anode	Expanded system
Global warming	kg $CO_{2eq.}$	0.53	0.33	0.20
Ionizing radiation	kBq Co-60 $_{eq.}$	0.38	0.38	0.17
Ozone formation, human health	kg $NOx_{eq.}$	0.41	0.39	0.20
Fine particulate matter formation	kg $PM_{2.5eq.}$	0.21	0.19	-0.07
Ozone formation, terrestrial eco	kg $NOx_{eq.}$	0.48	0.46	0.23
Terrestrial acidification	kg $SO_{2eq.}$	0.36	0.32	-0.18
Freshwater eutrophication	kg $P_{eq.}$	1.80	1.77	0.98
Marine eutrophication	kg $N_{eq.}$	0.008	0.008	0.001
Terrestrial ecotoxicity	kg 1.4-$DCB_{eq.}$	0.48	0.48	-0.43
Freshwater ecotoxicity	kg 1.4-$DCB_{eq.}$	10.05	9.96	2.51
Marine ecotoxicity	kg 1.4-$DCB_{eq.}$	7.96	7.89	2.2
Human toxicity (carcinogenic)	kg 1.4-$DCB_{eq.}$	212.51	211.77	205.90
Human toxicity (non-carcinogenic)	kg 1.4-$DCB_{eq.}$	0.18	0.18	0.09
Land use	m^2a crop$_{eq.}$	0.09	0.09	0.04
Mineral resource scarcity	kg $Cu_{eq.}$	0.002	0.002	0.001
Fossil resource scarcity	kg oil$_{eq.}$	1.13	1.13	0.69
Water consumption	m^3	1.48	1.48	1.27

Table D.3: Contribution to the endpoint impact categories (damage assessment, normalised and weighted)

Endpoint impacts				
Category	Unit	Carbon anode	Hydrogen anode	Expanded system
Damage assessment				
Human health	DALY	0.016	0.014	0.008
Ecosystems	species.yr	2.21E-05	1.71E-05	5.58E-06
Resources	USD2013	456	463	321
Normalised results				
Human health	-	0.687	0.608	0.353
Ecosystems	-	0.031	0.024	0.008
Resources	-	0.016	0.017	0.011
Weighted results				
Human health	Pt	272	241	140
Ecosystems	Pt	6.1	4.7	1.6
Resources	Pt	3.3	3.3	2.3

Appendix E

Sensitivity analysis results

Table E.1: Results for the sensitivity analysis of the electricity mix for the aluminium electrolysis process

Impact category	Units	Carbon anode system	Expanded H$_2$ anode system
Global warming	kg CO$_{2eq.}$	9 434	1 361
Ionizing radiation	kBq Co-60$_{eq.}$	2 841	-27
Ozone formation, human health	kg NOx$_{eq.}$	18.1	3.5
Fine particulate matter formation	kg PM$_{2.5eq.}$	13.3	-2.1
Ozone formation, terrestrial eco	kg NOx$_{eq.}$	18.3	3.6
Terrestrial acidification	kg SO$_{2eq.}$	34.8	-8.2
Freshwater eutrophication	kg P$_{eq.}$	6.5	0.5
Marine eutrophication	kg N$_{eq.}$	0.429	-0.006
Terrestrial ecotoxicity	kg 1.4-DCB$_{eq.}$	11 502	-8 873
Freshwater ecotoxicity	kg 1.4-DCB$_{eq.}$	423	-18
Marine ecotoxicity	kg 1.4-DCB$_{eq.}$	579	-0.06
Human toxicity (carcinogenic)	kg 1.4-DCB$_{eq.}$	2 488	2 091
Human toxicity (non-carcinogenic)	kg 1.4-DCB$_{eq.}$	12 370	2 071
Land use	m^{2}a crop$_{eq.}$	1 565	85
Mineral resource scarcity	kg Cu$_{eq.}$	192	169
Fossil resource scarcity	kg oil$_{eq.}$	2 521	626
Water consumption	m^3	119	-42

Table E.2: Results for the sensitivity analysis of the hydrogen production method, by methane steam reforming and water electrolysis.

Impact category	Units	Hydrogen anode system (hydro and wind power)	Hydrogen anode system (wind power)
Global warming	kg $CO_{2eq.}$	2 372	2 561
Ionizing radiation	kBq Co-60 $_{eq.}$	91	85
Ozone formation, human health	kg $NOx_{eq.}$	7.3	8.0
Fine particulate matter formation	kg $PM_{2.5eq.}$	4.3	5.1
Ozone formation, terrestrial eco	kg $NOx_{eq.}$	7.4	8.2
Terrestrial acidification	kg $SO_{2eq.}$	11.4	13.5
Freshwater eutrophication	kg $P_{eq.}$	1.04	1.39
Marine eutrophication	kg $N_{eq.}$	0.031	0.055
Terrestrial ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	5 638	17 312
Freshwater ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	206	799
Marine ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	288	1 010
Human toxicity (carcinogenic)	kg $1.4\text{-DCB}_{eq.}$	2 177	2 256
Human toxicity (non-carcinogenic)	kg $1.4\text{-DCB}_{eq.}$	5 283	8 027
Land use	m^2a $crop_{eq.}$	493	639
Mineral resource scarcity	kg $Cu_{eq.}$	186	196
Fossil resource scarcity	kg $oil_{eq.}$	735	792
Water consumption	m^3	550	19

Table E.3: Results for the sensitivity analysis of the fuel source for the HF production process

Impact category	Units	Expanded system with biofuel
Global warming	kg $CO_{2eq.}$	1 768
Ionizing radiation	kBq Co-60 $_{eq.}$	82
Ozone formation, human health	kg $NOx_{eq.}$	4.0
Fine particulate matter formation	kg $PM_{2.5eq.}$	-1.8
Ozone formation, terrestrial eco	kg $NOx_{eq.}$	4.1
Terrestrial acidification	kg $SO_{2eq.}$	-7.5
Freshwater eutrophication	kg $P_{eq.}$	-0.64
Marine eutrophication	kg $N_{eq.}$	0.004
Terrestrial ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	-6 775
Freshwater ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	63
Marine ecotoxicity	kg $1.4\text{-DCB}_{eq.}$	100
Human toxicity (carcinogenic)	kg $1.4\text{-DCB}_{eq.}$	2 121
Human toxicity (non-carcinogenic)	kg $1.4\text{-DCB}_{eq.}$	2 634
Land use	m^2a $crop_{eq.}$	155
Mineral resource scarcity	kg $Cu_{eq.}$	172
Fossil resource scarcity	kg $oil_{eq.}$	731
Water consumption	m^3	339

Table E.4: Results for the sensitivity analysis of the energy source for the aluminium oxide production method

Impact category	Units	Carbon anode system (wind and solar power)	Hydrogen anode system (wind and solar power)
Global warming	kg $CO_{2eq.}$	7 033	5 398
Ionizing radiation	kBq Co-60 $_{eq.}$	505	502
Ozone formation, human health	kg $NOx_{eq.}$	16.9	16.5
Fine particulate matter formation	kg $PM_{2.5eq.}$	13.6	13.1
Ozone formation, terrestrial eco	kg $NOx_{eq.}$	17.6	17.2
Terrestrial acidification	kg $SO_{2eq.}$	30.2	28.6
Freshwater eutrophication	kg $P_{eq.}$	4.4	4.3
Marine eutrophication	kg $N_{eq.}$	0.373	0.371
Terrestrial ecotoxicity	kg 1.4-$DCB_{eq.}$	126 338	126 360
Freshwater ecotoxicity	kg 1.4-$DCB_{eq.}$	2 640	2 637
Marine ecotoxicity	kg 1.4-$DCB_{eq.}$	3 344	3 341
Human toxicity (carcinogenic)	kg 1.4-$DCB_{eq.}$	2 925	2 918
Human toxicity (non-carcinogenic)	kg 1.4-$DCB_{eq.}$	24 306	24 256
Land use	m^2a $crop_{eq.}$	3 596	3 589
Mineral resource scarcity	kg $Cu_{eq.}$	306	305
Fossil resource scarcity	kg $oil_{eq.}$	1 666	1 671
Water consumption	m^3	518	518