Master's thesis

NTNU
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Life Cycle Assessment of silicon metal by aluminothermic reduction: an industrial symbiosis approach

Master's thesis in Circular Economy
Supervisor: Johan Berg Pettersen
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The following is the original problem description of this research. During the course of the master thesis, this was slightly adapted from the original according to the reality of the data that has been obtained up to this moment, since the experimental modelling is currently ongoing.

> Silicon is a Critical Raw Material (CRM) of high importance and high risk associated with its supply in Europe. The H2020 project SisAl Pilot is a novel process that aims to test the replacement of the conventional production of silicon, which uses carbon reductants and quartz as a silicon source, with an aluminothermic reduction using secondary aluminium and silicon raw materials instead, intending to ensure the supply while at the same time costs are reduced and the environment is better protected. This Master Thesis will build on the Specialization Project that was developed during the Autumn semester. In this research, a first-order inventory model, LCA and contribution analysis was developed to evaluate both the conventional production of silicon and SisAl process. Results showed that an aluminothermic reduction as performed in the SisAl route would potentially reduce the impact on climate change, carcinogenic human toxicity, photochemical ozone formation and terrestrial and marine eutrophication, when using post-consumer aluminium scrap as an input. However, the rest of the impact categories studied performed better following the conventional (carbothermic) route. The increased impact of the aluminothermic production in some impact categories was attributed to the following hotspots identified: the input of post-consumer aluminium scrap and the emissions of the furnace. Both present an opportunity for further reduction. First, the input of post-consumer aluminium scrap could be substituted by the input of aluminium dross. A sensitivity analysis on the effect of this substitution showed that most impact categories would then decrease substantially. However, the lack of data on the emissions of this process did not allow for a further investigation and a more precise calculation. Secondly, the emissions obtained in the furnace were overestimated since data was not accessible for the aluminothermic production of silicon, and a worst-case scenario was applied in which all the trace metals entering the furnace in the raw materials escaped through the fumes when their boiling point was above the process temperature. Now that experimental data have been obtained by other research institutions of the SisAl Pilot, this Master Thesis will develop a more comprehensive LCA of the existing model, with possible extensions being aluminium dross as an input, the use of various Si feeds, and future scenarios of waste flows, silicon products, energy, etc.

Abstract

Silicon is a Critical Raw Material of high economic importance that also faces a great supply risk in Europe. Conventionally, silicon is produced by reducing quartz with carbon, in a process known as carbothermic reduction of silicon. In this master thesis, a new approach that substitutes carbon reductants and primary materials by former aluminium and silicon waste streams is benchmarked. This production route, the aluminothermic reduction of silicon, could be more sustainable from an environmental perspective as it can reduce both furnace emissions and the overall electricity consumption of the process. A Life Cycle Assessment (LCA) is therefore developed to compare the sustainability of the conventional and aluminothermic silicon production routes. Different secondary input materials are explored in the aluminothermic route, for instance, the use of aluminium dross, post-consumer aluminium scrap or silicon skulls, and the influence of future scenarios is evaluated. Results show that the impact decrease substantially in the aluminothermic route for most studied impact categories, when new scrap is utilized as raw material, following a reduction in the energy consumed, pollutants emitted and enhanced waste utilization rate. However, the use of post-consumer aluminium scrap is dependent on the expected alternative use of the scrap fraction and could account for much higher impacts when applying a global scope. In the coming years, future scenarios show a great opportunity in the aluminothermic route as an example of industrial symbiosis for these raw material industries, following surplus volumes of aluminium scrap and an increased demand for silicon metal.

Abstract translation to Spanish

El silicio es una materia prima crítica de gran importancia económica pero que también sufre un alto riesgo de suministro en Europa. De manera convencional, el silicio se produce mediante la reducción de cuarzo con carbono, en un proceso conocido como reducción carbotérmica. En esta tesis, se analiza un nuevo proceso industrial, la reducción aluminotérmica, que tiene como objetivo sustituir estos materiales por materias primas secundarias de la industria del aluminio y del silicio, lo que podría constituir una alternativa más sostenible desde el punto medioambiental, ya que disminuyen tanto las emisiones del horno como el consumo de electricidad del proceso. En este estudio se aplica un Análisis de Ciclo de Vida (ACV) para la comparación del impacto ambiental entre ambas rutas de producción, considerando diversas materias primas en la ruta aluminotérmica como la escoria de aluminio, chatarra o el cuarzo en escoria, explorando la influencia de futuros escenarios en el proceso. Los resultados indican que el impacto disminuye sustancialmente para la mayoría de las categorías de impacto, cuando se utiliza chatarra nueva de acuerdo con una reducción en el consumo de energía, los contaminantes emitidos y un mayor aprovechamiento de los residuos. Sin embargo, el impacto de aplicar chatarra vieja depende del uso alternativo de esta fracción de residuos, y puede alcanzar una mayor contribución cuando se considera un alcance global. Futuros escenarios que predicen un exceso en el volumen de residuos de aluminio y un aumento de la demanda de silicio muestran una gran oportunidad en el establecimiento de la simbiosis industrial en las industrias del silicio y aluminio siguiendo la ruta aluminotérmica.

Acknowledgements

This master thesis would not have been possible without the expertise, wise advice, encouragement, and patient supervision of Johan Berg Pettersen. I am extremely grateful for your belief in me and feel lucky to work with you. I would also like to recognize the assistance and thank my co-supervisor Yan Ma, for her insights on the metallurgical processes.

I wish to extend my gratitude to the SisAl Pilot Consortium for providing me with the details of this innovative process, and for bringing me the opportunity to take part in this project. I would like to give special thanks to Alejandro Abadías Llamas, for his continuous help through this research and positive words.

I am thankful, as well, to all the wonderful people that I have met in this journey that started two years ago. My friends from Chalmers University of Technology and the Norwegian University of Science and Technology, the Indecol students, my companions in the study room, and particularly to Caro, for all the happy moments. Thanks to all the professors and researchers from these institutions that have taught me so much, and an extra thanks to Ulrika Lundqvist, for her valuable guidance throughout my studies.

In addition, I would like to thank Asier Sopelana, who first introduced me to the world of Life Cycle Assessment.

Last but not least, I wanted to thank my amazing family and friends that have always been there, for their endless support.

The project has received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement N° 869268.

Contents

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List of abbreviations and symbols

Al	Aluminium
Al_2O_3	Aluminium oxide (alumina)
ALCA	Attributional LCA
AoP	Areas of Protection
APOS	Allocation at Point of Substitution
As	Arsenic
C	Carbon
$CaCO_3$	Limestone
CaO	Calcium oxide
CF	Characterization factor
CG-Si	Chemical grade silicon
CH_4	Methane
CLCA	Consequential LCA
CO_2	Carbon dioxide
Cu	Copper
CRM	Critical Raw Material
DCB	Dichlorobenzene
DS	Degree Scenario
EG-Si	Electronic grade silicon
eq.	Equivalent
ETS	Emissions Trading System
EU	European Union
Fe	Iron
Fe_2O_3	Iron (III) oxide
F.U.	Functional Unit
GDP	Gross Domestic Product
GHG	Greenhouse gas
GLO	Global, as in ecoinvent
GWP	Global Warming Potential
(H/A)	Hierarchist approach, average weighting
H^+	Hydron
H_2O	Water
Hg	Mercury

H2020	Horizon 2020
IEA	International Energy Agency
IRP	Ionizing Radiation Potential
ILCD	International Reference Life Cycle Data system
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
Li	Lithium
MG-Si	Metallurgical grade silicon
Mn	Manganese
N	Nitrogen
N_2O	Nitrous oxide
NMVOCs	Non-methane volatile organic compounds
NO	Norway, as in ecoinvent
NOx	Nitrogen oxides
O_2	Oxygen gas
P	Phosphorus
PAHs	Polyciclic Aromatic Hydrocarbons
PMs	Particulate Materials
Pt	Weighted points
PV	Photovoltaic
R	Yield
RER	Europe, as in ecoinvent
RoW	Rest-of-the-World, as in ecoinvent
S	Sulfur
SAF	Submerged Arc Furnaces
Se	Selenium
Si	Silicon
SiO	Silicon oxide
SiO_2	Silicon dioxide
SOG-Si	Solar grade silicon
SOx	Sulfur oxides
SO_2	Sulfur dioxide
SOP	Surplus Ore Potential
SPL	Spent Pot Lining
TP	Toxicity Potential
U	Unit, as in ecoinvent

“The enormous appetite for resources (energy, food, and raw materials) is putting extreme pressure on the planet, accounting for half of the greenhouse gas emissions and more than 90% of biodiversity loss and water stress. Scaling up the circular economy will be vital to achieve climate neutrality by 2050, while decoupling economic growth from resource use and keeping resource use within planetary boundaries.”

—European Commission, *Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability (2020)*.

Chapter 1

Introduction

1.1 The sustainability of silicon and aluminium in Europe

With climate change threatening global ecosystems, a shift towards a low-carbon economy is essential, and some raw materials are key enablers of this transition.

One of these elements is silicon. Silicon plays a strategic role in the reduction of greenhouse gas (GHG) emissions as it is the major component of photovoltaic systems, and widely used in Li-ion batteries to increase their capacity and in the electronics industry as a semiconductor [1]. In the chemical industry, it is the starting point of silicones, which can also help to bring down carbon dioxide (CO_2) emissions across many sectors, from improving the energy performance of buildings by providing better insulation to protecting devices thanks to their thermal moisture and water resistance, making products last longer [2]. The other main market for silicon metal is in its application for alloying aluminium, to improve its fluidity, resistance to hot cracking and pressure tightness [3].

Aluminium and aluminium alloys are also necessary materials for this transition. Because of its lightweight properties combined with cost efficiency, recyclability and high specific strength, aluminium is becoming an alternative to other traditionally used metals such as steel, cast iron and titanium in certain applications where the concern for fuel efficiency, emission requirements and consumption of raw materials is increasing [4].

However, assessing the sustainability of materials such as aluminium and silicon from an environmental, economic, and social perspective is a complex issue. While these materials allow for lower emissions in the use phase for many human activities, their production processes also contribute to the environmental impacts related to energy consumption, emissions and wastes generated [5–8]. Besides, the availability of silicon is compromised: while silicon is an abundant element in the

Earth's crust, the fact that silicon metal cannot be substituted in many applications and that there is no recycling of pure silicon, together with a dependency on other countries to supply this metal, has placed it inside the list of Critical Raw Materials (CRMs) for the European Union (EU) [9].

Critical metals are economically important but from geopolitical and environmental perspectives also face supply risks [10]. Europe is overall a net importer of silicon, as it produces below 10% of the total production [11]. The EU self-sufficiency for silicon is only established at 31,8%, meaning that even if 100% of silicon was recycled the EU would still not be self-sufficient [12]. In contrast, China accounts for more than two-thirds of the global production worldwide [13]. An explanation for this difference can be found in the strong environmental, social and financial standards that the European silicon sector abides which do not bear comparable costs as faced by other third-country producers (for instance, regarding the EU-ETS scheme) [1]. As silicon forms a stable compound with oxygen (silicon dioxide, or SiO_2) and its deoxidization consumes substantial energy, the associated environmental costs are high, especially because some industries require a high purity rate of this material [14].

A sustainable material society works hand in hand with energy efficiency and low-carbon intensity, and therefore it is essential to utilise raw materials in a circular manner preventing their depletion and associated increased prices that could, in turn, affect its future use. In this context, the project H2020 "SisAl Pilot" intends to demonstrate a novel process with the potential to replace the conventional reduction of silicon (using carbon reductants and quartz as raw materials) with an aluminothermic reduction, which uses silicon and aluminium secondary materials instead. This approach would potentially benefit the silicon and aluminium industries through industrial symbiosis, by reducing the environmental impact of both industries as well as facilitating independence from other countries to supply silicon metal. Furthermore, the export of aluminium scrap would be reduced, and Europe is also a major exporter of these residues [15].

With many studies predicting an increase in the silicon demand for the coming years [e.g. 9], the time could not be better to explore the potential of circular economy in the silicon and aluminium industries from a life cycle perspective, protecting natural resources and reducing the severity of the environmental problems caused by their use. Besides, the fact that the aluminium industry acts as both the raw material supplier and end-user in many applications of silicon could facilitate the exchange of materials and information between these industries, and contribute even more strongly to circularity [16].

Over this chapter, the conventional production of silicon and the SisAl Pilot routes are explored (Chapters 1.2 and 1.4) to better appreciate the differences. The production route for aluminium products will also be addressed (Chapter 1.3) as the provider for the reductants used in the aluminothermic reduction.

Life Cycle Assessment (LCA) will then be introduced as a tool to measure the sustainability and trade-offs of the different systems to produce silicon, and the main goal, specific objectives and research questions will be defined (Chapter 1.5).

1.2 The conventional production of silicon metal and off-grades

The conventional or carbothermic production of metallurgical grade silicon is performed by reducing silicon dioxide with carbon in Submerged Arc Furnaces (SAF). A schematic representation of the SAF furnace and the typical configuration of a production plant for silicon can be observed in Figure 1.1.

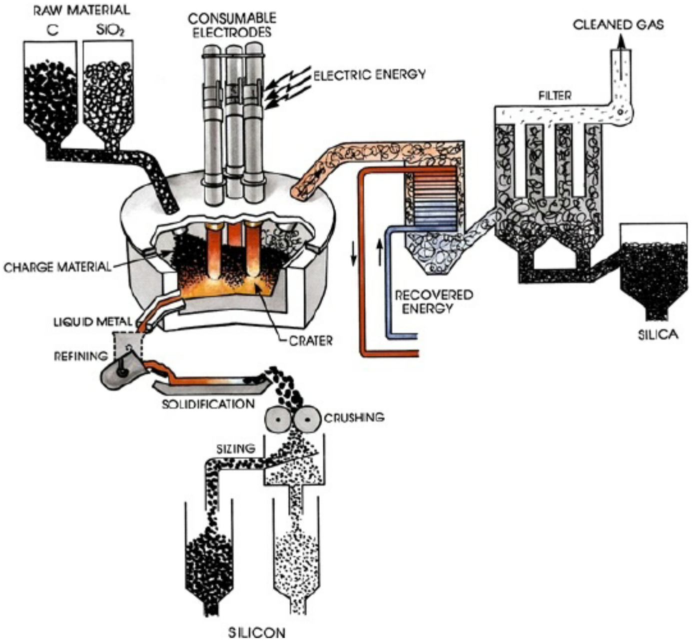

Figure 1.1: Representation of a typical plant for the production of silicon metal. Source: “Production of high silicon alloys" [17].

In this process, a mixture of quartz (crystalline silicon dioxide - SiO_2) and carbon reductants is charged from the top of the furnace (the low-temperature zone) and heated employing the electric arc and electric ground of the furnace; silicon metal is then tapped from the bottom of the furnace (high-temperature zone) [18]. Under equilibrium conditions, there will always be a loss of silicon in the form of silicon oxides (SiO) [19]. In the end, the reaction with oxygen after the furnace will cause the formation of silica fume (non-crystalline SiO_2, the ultrafine powder collected after the furnace) and carbon dioxide (CO_2), as in Equation 1.1 in the following page [17].

The yield R (Equation 1.2), or the parameter that expresses the silicon oxide that is successfully turned into silicon metal, is connected with the furnace operation and raw material properties [20].

$$(1+x)SiO_2 + (2+x)C + (1+x)O_2 \rightarrow Si + xSiO_2 + (2+x)CO_2 + heat \tag{1.1}$$

$$x = \frac{1-R}{R} \tag{1.2}$$

Besides the emissions of carbon dioxide and silica fume, other gases released from the furnace are methane (CH_4), nitrogen and sulfur oxides (NOx and SOx), polycyclic aromatic hydrocarbons (PAHs), or heavy metals contained in the raw materials and electrodes, as well as dust, which is produced in almost every step of the process [21].

A heat exchanger placed after the furnace can recover approximately 20% of the energy that was contained in the leaving gases [19]. The off-gas is then conducted through a filter, allowing the recovery of amorphous SiO_2(condensed silica fume) [17].

Silicon is classified into the following categories according to the purity of the metal: metallurgical grade silicon (MG-Si), chemical grade silicon (CG-Si), solar grade silicon (SOG-Si) and electronic grade silicon (EG-Si) [22]. The product obtained in the SAF is metallurgical grade silicon, which is used in alloying aluminium and steel but not suitable for other applications, needing further purification methods and a higher purity [18]. Silicon materials in the chemical industry usually display more than 99% Si purity [23], while in the semiconductor industry the impurities are in the ppb and ppm range for the electronic devices and photovoltaic cells, respectively [17]. In Table 1.1, the different grades of silicon are summarised. Figure 1.2, on the next page, depicts the production chain for the different grades and end-uses of silicon.

Table 1.1: Summary of silicon grades.

Name	Si content	Applications
Metallurgical grade silicon (MG-Si)	98-99%	Alloying of aluminium and steel.
Chemical grade silicon (CG-Si)	>99% purity	More than 10.000 applications (e.g. silicones).
Electronic grade silicon (EG-Si)	Impurities in the ppb range	Electronics.
Solar grade silicon (SOG-Si)	Impurities in the ppm range	Solar cells.

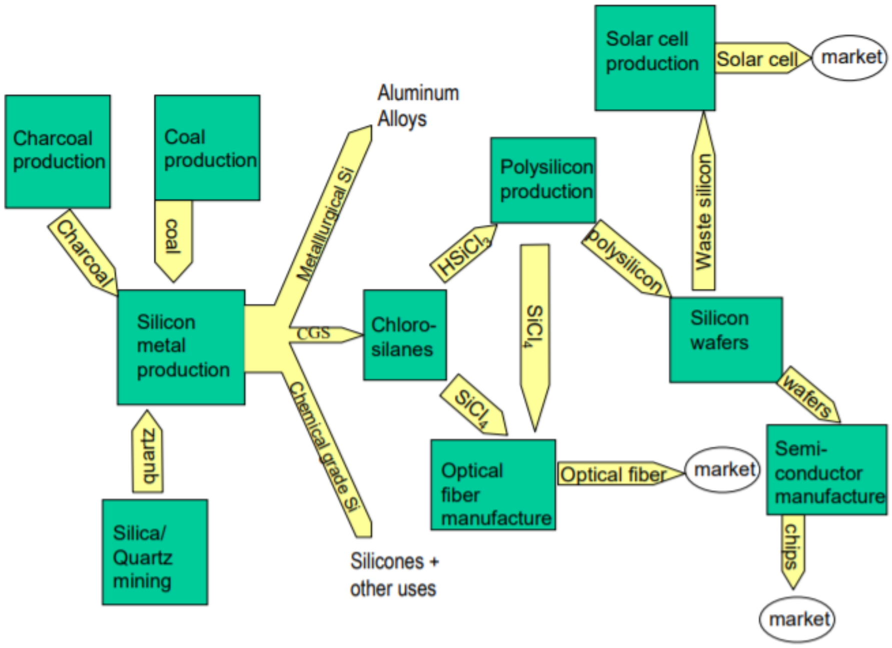

Figure 1.2: Production chain for the different silicon material grades. Source: "Global production chains and sustainability: the case of high-purity silicon and its applications in IT and renewable energy" [24].

Some purification methods of MG-Si include tapping of the molten silicon into a refining ladle, and then treatment with oxidative gas and slag-forming additives, an operation that involves large heat losses [25]. Impurities are captured into the slag phase and are then removed before the next batch of silicon is tapped, still some solidified materials are not removed and remain on the surface of the ladle, known as silicon skulls [26]. This by-product is today sold at a low price to silicomanganese-alloy producers [27].

For the obtention of the highest purity silicon for the semiconductor industry, further refining needs to be applied. One purification method is the Siemens batch-wise process, where metallurgical grade silicon is hydrochlorinated to form trichlorosilane, followed by a fractional distillation [18]. Another purification route was developed in Elkem, with lower energy use [19].

After the desired purity of silicon has been achieved, it goes through casting in molds and cooling, and then it can be subject to crushing, screening and packing before being sent to the customer [28].

A flowchart picturing the life cycle of silicon is included in Figure A.1 (in Appendix A). Note that silicon metal is not generally being recovered from post-consumer waste, mainly due to its disperse use [29].

1.3 Aluminium primary and secondary production

The life cycle of aluminium begins when it is mined as bauxite (mainly $Al_2O_3 \cdot H_2O$), but also containing Fe_2O_3, SiO_2 and other impurities [19]. The Bayer process extracts the alumina (Al_2O_3) by caustic digestion followed by clarification, precipitation, washing and calcination [30]. Red mud (or bauxite residue) is a hazardous waste released from this process which owes its red colour to a high content in iron [31].

The alumina is then transported to aluminium smelters where electrolysis is applied in a process known as Hall-Héroult [30]. The hazardous solid waste from the electrolysis is called Spent Pot Lining (SPL) and contains a high amount of fluoride salts and toxic cyanides [32]. When molten aluminium is formed, it comes in contact with air in its outer surface and therefore is subject to oxidation, producing white dross (in primary smelters) and black dross (in secondary industry sectors, after the treatment of white dross) [33]. Dross is also considered a hazardous material, able to irritate skin and eyes and precursor of ammonia and other gases [30, 34]. The dross with higher recoverable aluminium content (between 15 and 20%) is called white dross, and black dross displays a mixture of aluminium oxide and less than 10% metallic aluminium [33]. Because the concentration of aluminium in dross has the most significant impact on the electricity consumed and revenues generated in the recycling process [35], white dross can be valorised in the secondary steel industry or secondary aluminium production [36], whereas black dross is more difficult to extract [34].

After its use, aluminium post-consumer scrap can be recycled to reduce the energy intensity of primary production between 90% and 95% [37]. A diagram showing the life cycle of aluminium is displayed in Figure A.2 in Appendix A.

1.4 The SisAl Pilot

An aluminothermic reduction of silicon as described in the SisAl Pilot intends to produce silicon in a more environmentally beneficial approach, as the use of primary carbon reductants and quartz raw materials is avoided through utilizing residues from the silicon and aluminium industries. Calcium oxide (CaO) is also added to this process but partly recovered and recirculated in the system. The aluminothermic reduction of silicon takes place through the following reaction:

$$SiO_2 \text{ (in } CaO - SiO_2 \text{ slag)} + 4/3Al \rightarrow Si + 2/3Al_2O_3 \text{ (in } CaO - Al_2O_3 \text{ slag)} \quad (1.3)$$

As pictured in Figure 1.3 below, the process can be summarised into three steps:

1. Silicon dioxide (if possible, in the form of secondary materials such as silicon skulls or Si fines) and CaO are combined in a vessel, and the slag of molten calcium silicate ($CaO \cdot SiO_2$) is formed.

2. Aluminium metal (from secondary sources, e.g. Al scrap, dross...) is introduced to reduce calcium silicate slag to Si metal and forming a calcium aluminate slag.
3. In the final step, the $CaO\text{-}Al_2O_3$ slags are separated through a hydrometallurgical process (alkaline leaching). The $CaO{\cdot}SiO_2$ residue is then returned for its application in process 1, partially replacing the need for further CaO.

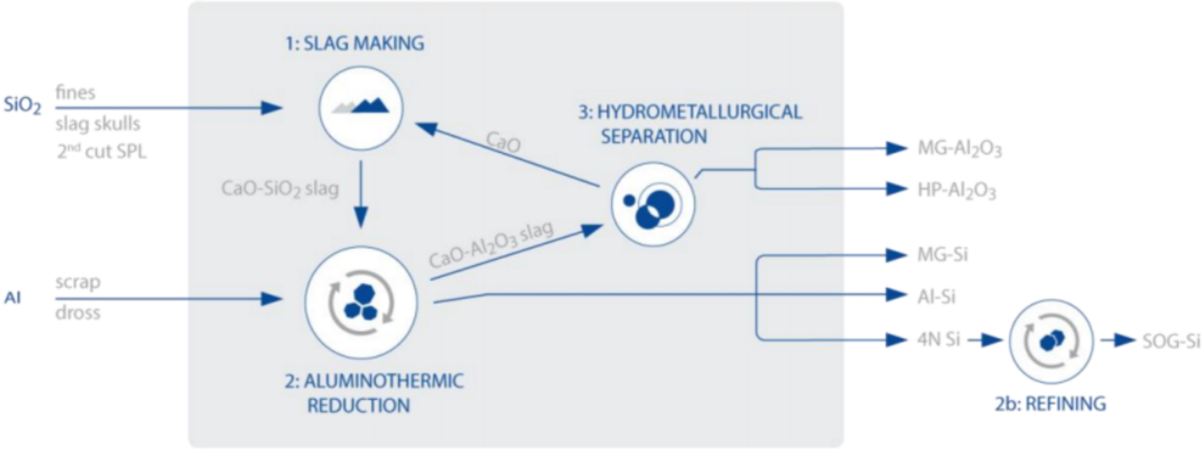

Figure 1.3: Schematic representation of the aluminothermic production route. Source: SisAl Pilot [27].

Upgrading the off-grades from silicon and aluminium production could both decrease the waste streams (hazardous in the case of some aluminium residues) as well as the emissions associated with the production of silicon since the new reductants do not rely on organic materials. A preliminary evaluation of the SisAl process [27] predicts that pollutants such as CO_2, CH_4, PAHs and SO_2 are minimal since the combustion of carbon raw materials will be avoided. Besides, NOx is also reduced as these gases are only produced in the combustion of SiO gas with air, and less SiO gas is being created (only at tapping). Most Particulate Materials (PMs) are also avoided in the aluminothermic process because the reduction to SiO_2 goes directly from Si without the need to combust SiO gas. Another group of pollutants that would be potentially reduced are some heavy metals that originate from the carbon raw materials as these are not included in the aluminothermic reduction.

However, other pollutants could be derived from the application of the aluminothermic route if, for instance, the secondary materials used contain different metals or other impurities that were not associated with the carbothermic route. The impact of the aluminothermic route for silicon production could also be higher than in the conventional route if the production of the raw materials consumed accounted for greater impacts in the different impact categories. It is therefore necessary to evaluate this potential effect of the SisAl production route to ensure that it proves advantageous from an environmental perspective along the life cycle and to apply corrections, if necessary, to minimize the negative externalities before these systems are applied on a larger scale.

1.5 Research questions and application of LCA

A Life Cycle Assessment (LCA) is conducted in this study to evaluate the potential environmental benefits and trade-offs of this new route for the production of silicon (i.e. the aluminothermic reduction), in comparison with the conventional silicon production route. The environmental performance of both routes under different scenarios of aluminium waste flows and silicon products is investigated using a system perspective.

By including the impact of a product or service over its entire life cycle, from the raw materials acquisition, production, transport and use to the end-of-life, the application of LCA allows a comparison between the different production systems studied. The inputs and outputs to each stage in the life cycle of a product cause an environmental impact and when applying LCA it is possible to compare the alternatives and find the hotspots of pollution in the associated objects of concern. This integrative approach is intended to avoid burden shifting between life cycle stages or impact categories, i.e. when by lowering the environmental impact in one part of the system other environmental impacts may be created (sometimes even larger). One example would be in energy systems when the electricity comes from nuclear power, decreasing the climate change impact but increasing the potential radioactive emissions.

A relevant outcome of the application of LCA stems from the readability and comparability of the environmental metrics, because the inventory, containing many different inputs and outputs, is aggregated and "translated" into potential impacts that can be easily interpreted. The results of this study intend to allow for an informed decision in the aluminium and silicon industries regarding which production system is more beneficial from a sustainability perspective. Besides, as the major contributors of pollution are identified in both systems, this paves the way for the implementation of the necessary changes to prevent harmful consequences in the SisAl production, if any raw material is identified as detrimental to the environment.

However, a downside of the LCA methodology is that the high level of aggregation that makes it so useful also hides many assumptions and uncertainties that are piled up into a few categories' results. The uncertainty in LCA studies is therefore substantial and needs to be assessed in every study.

The application of the LCA methodology for the study of the silicon production routes is described with further details in Chapter 3.

The main aim of this thesis is to benchmark the lifecycle environmental performance of silicon produced by aluminothermic reduction, and in particular, the effect of resourcing former waste streams for silicon and aluminium as raw materials for this process, to support the decision-making process enhancing the environmental performance of silicon and aluminium industries.

The specific objectives are:

- To develop the LCA of the aluminothermic reduction process, considering silicon skulls and aluminium dross as raw materials for this production route, and comparison with the conventional (carbothermic) reduction, identifying hotspots of pollution and possible improvements.
- To test the influence of the application of other raw materials and different geographical conditions on the environmental performance of the conventional and aluminothermic reduction processes.
- To perform scenario analyses to study how different conditions in the future might affect the contribution to the environmental impact of silicon production.

Therefore, the research questions connected to the above objectives and main aim of this study are:

- What are the life cycle characteristics of the carbothermic and aluminothermic production of silicon (using silicon skulls and aluminium dross) in Norway, and the different contribution to the environmental impact between these alternatives?
- How sensitive is the environmental impact of silicon production to the raw materials feed and changes in the electricity mix?
- How does the application of the SisAl Pilot further reduce the environmental impact of the silicon industry when considering future scenarios of aluminium waste flows and silicon demand?

The systems studied and the main reactions occurring in each furnace are represented in Figure 1.4.

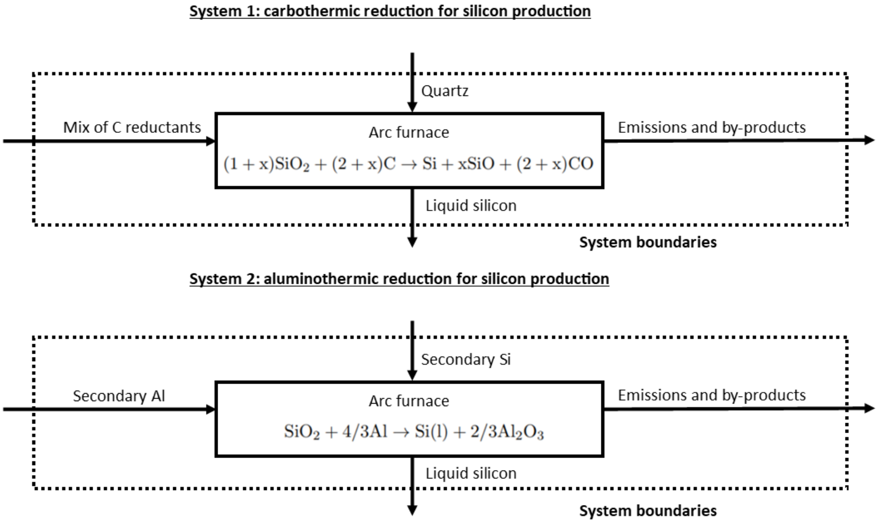

Figure 1.4: System flowcharts. The different reduction processes for the silicon production are depicted, along with the inputs used in this assessment. Note that for simplicity only the foreground system (i.e. the processes under the control of the decision-maker for whom the LCA is carried out) is included.

The structure followed in the thesis is summarised below:

- Throughout **Chapter 1: Introduction**, the complex assessment of the sustainability in silicon and aluminium industries has been introduced, together with an overview of the life cycles of both silicon and aluminium production routes and to the SisAl process. The aim, objectives, research questions and application of LCA in the context of this study have been described.
- In **Chapter 2: Previous work and future trends**, previous work regarding the application of LCA in the silicon and aluminium industries is identified and discussed. Besides, other examples of utilization of silicon and aluminium wastes as raw materials are outlined, setting the aluminothermic production in context. Chapter 2 ends with a literature review of future scenarios for silicon and aluminium waste flows, as well as of other parameters that could drive the systems of study (e.g. regulatory, due to material scarcity. . .).
- In **Chapter 3: Material and methods**, the application of Life Cycle Assessment is described in detail for the context of this research. The contextual and modelling aspects of this LCA, such as e.g. the goal definition, functional unit, system boundaries or impact categories are defined.
- **Chapter 4: Results and discussion** develops the impact assessment and contribution analysis for the different impact categories. The uncertainty and sensitivity analyses and scenarios are also developed and interpreted.
- **Chapter 5: Conclusion.**

Chapter 2

Previous work and future trends

Handling the secondary streams of both aluminium and silicon metal production as well as the end-of-life residues is becoming increasingly important, to give an answer to an increased demand for these materials and sustainably handle their residues.

As it has been discussed during Chapter 1.3 the market for aluminium metal relies heavily on recycling secondary aluminium. To dilute the unwanted elements, primary aluminium is mixed with the stream of aluminium residues in a process known as cascade recycling. As aluminium loses quality, the transportation sector acts as a final sink, potentially leading to a scrap surplus of these residues in the future [38]. On the other hand, the residues generated in the production of aluminium also involve many hazardous wastes (e.g. red mud, SPL), that are not usually recycled [39].

Regarding the silicon residues, as it was analysed in Chapter 1.2, the recycling of post-consumer silicon is considered negligible, and the scrap generated during the production process (new scrap) such as silicon skulls is generally sold to the Si-Mn alloy industry.

The aluminothermic reduction has been considered before as an alternative route for the production of silicon [40]. However, the approach of the SisAl Pilot is to use secondary materials as inputs for this process, which would turn it into more economically viable, as residues do not hold a significant value, but potentially also more environmentally responsible, converting the linear production system into a circular ecosystem for aluminium and silicon producers and waste handlers.

Previous studies regarding silicon and aluminium waste as raw materials have seized the opportunity for aluminium dross acting as a degasser in steel casting [41] or as a filler material in asphalt [42]. Silicon slags, for instance, could also be valuable in the glass-ceramics industry [43]. Global efforts across multiple sectors are required to address sustainability in the metal industry, and the SisAl Pilot wants to contribute to these approaches in closing the gap of sustainable consumption and production, supported by the mutual interest of both aluminium and silicon industries.

When looking at the impacts of the conventional production of silicon and aluminium, the most relevant impact categories for these industries are found in climate change, ecotoxicity, human toxicity, particulate matter formation, fossil resources and acidification [5, 7]. Besides, electricity consumption is identified as a large contributor to both systems [6, 7]. In the aluminium industry, the handling of red mud also contributes significantly to the environmental impact in terms of waste management [8]. These impacts, which are further explained during the Scope definition (Chapter 3.2.2), are essential in the assessment of the sustainability of both conventional and aluminothermic production routes.

To be able to study the future implications of the conventional and aluminothermic production routes, a literature review was conducted looking at the trends and scenarios for silicon demand and aluminium waste flows in the coming years. The main key arguments in this literature review can be found below.

The market for silicon metal is currently dominated by its use in the alloying of aluminium and other metals (more than 40%), followed by silicones (and other CG-Si applications) and finally in the solar and semiconductor industry (see Figure 2.1).

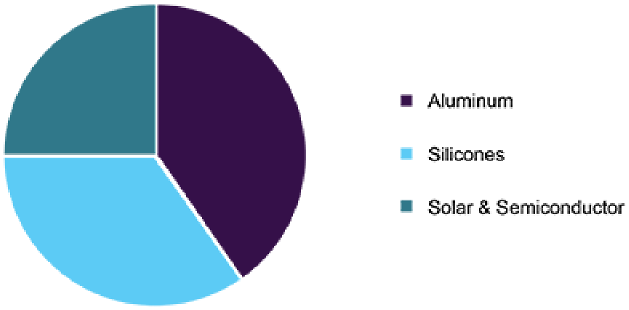

Figure 2.1: Global silicon metal revenue share, by application. Data for 2019 from Grand View Research [44].

The silicon market involves a vast spectrum of applications ranging from the more traditional uses in the raw material sector to new markets in semiconductor devices and optical fibres, in the transition to a digital economy. The many applications of silicon make it also difficult to assess the future demand of this material (for instance, silicones are used in more than 10.000 individual applications, according to Roskill [45]). However, it is clearer that an expanding presence of silicon in end uses such as solar and renewable energy technologies, personal care, silicones, electronics, or the alloying of aluminium can be expected, where developing countries could drive future demand [45]. The prospects for the different silicon technologies and purities of this material are explored and discussed below.

Regarding solar-grade silicon for solar panel technologies, the World Bank report on the “Growing role of minerals and metals for a low carbon future” [46] states that solar photovoltaic (PV) technologies will rapidly increase under all future projections (see Figure 2.2). Crystalline silicon cells currently make up about 85% of the market, and future studies assume most solar PV installations will be of this variety also in the future [46]. This increase in demand is related to decreasing prices explained by the experience curve [47]. On the other hand, the amount of polysilicon that is required per unit produced has dropped due to technological advances that have allowed for thinner wafers and less waste generated [48].

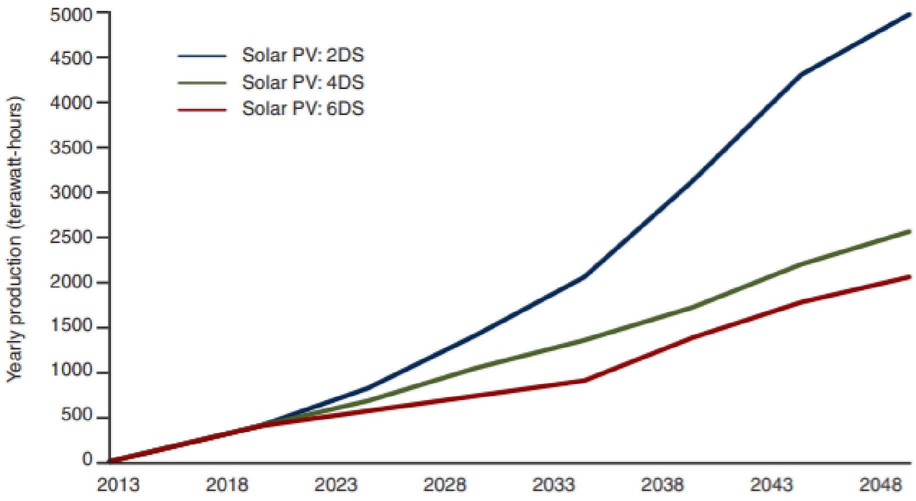

Figure 2.2: Solar PV electricity production (yearly electricity supply scenarios) Note: DS = degree scenario. Source: “Growing role of minerals and metals for a low carbon future" [46]. Scenarios proposed by the International Energy Agency (IEA) [49].

Another segment of refined silicon consumption is found in the electronics and silicones industries. Today’s electronic industry is made possible by the silicon contained in computer chips used in electronics such as mobile phones, computers or refrigerators. Electronic-grade silicon is likely to keep experiencing a growth in demand in the coming years, driven by storage and cloud computing, communication devices, automotive and industrial electronics, as well as emerging technology like artificial intelligence and 5G networks [50]. However, other semiconductor materials may become part of this future market paradigm [51]. Similarly, chemical-grade silicon future demand, with many applications such as e.g. silicon oils and grease, sealants, cosmetics, resins, pastes, etc. is also difficult to assess. Some authors have tackled this problem assuming that the growth rate is constant over the years [52]. A large part of silicones consumption is a consequence of disposable income and thus related with the consumers' purchasing power, with a high growth potential regarding developing countries and an increasing middle-class [45]. The annual growth potential for silicones is estimated to be over 4% during 2019-24, outpacing Gross Domestic Product (GDP) growth [53].

The remaining major market for silicon is found in the metallurgical-grade silicon for the alloying of the aluminium industry. Aluminium growth is forecasted to grow in the near future (see Figure 2.3) with many sectors driving this demand as the transportation sectors, buildings, packaging... (Figure 2.4).

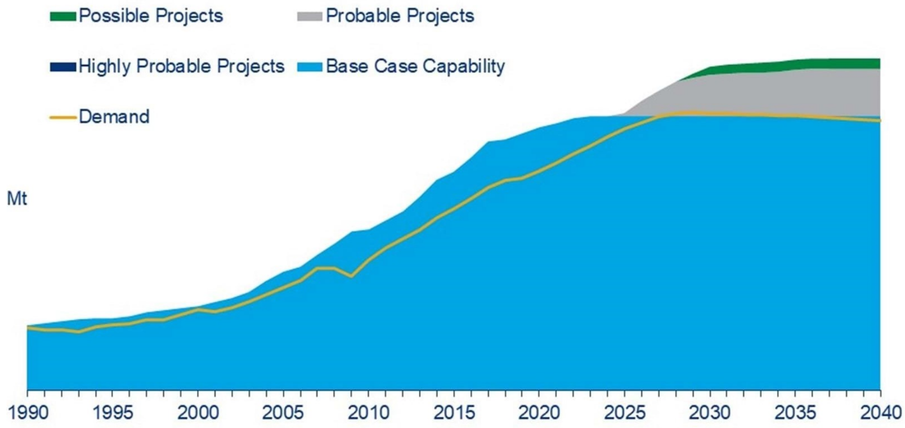

Figure 2.3: Aluminium demand forecast to 2040. Source: Wood Mackenzie [54].

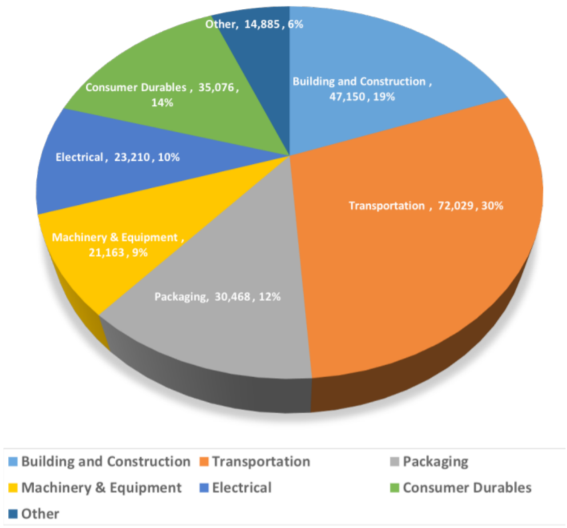

Figure 2.4: Predicted aluminium demand by sector in 2050. Unit: Kilo-Tonnes Per Annum (ktpa) and %. Source: CM Group [55].

With an increased aluminium and silicon production, the wastes generated in these industries are also expected to rise. Nowadays, the production of silicon and aluminium releases an equivalent of 45.000 tonnes of silicon skulls per year and between 60.000 and 80.000 tonnes of aluminium dross per year, respectively, and the post-consumer aluminium scrap net export ascends to more than 900.000 tonnes per year only in Europe [27].

Other factors influencing the environmental performance of silicon and aluminium production industries in the future will most likely be driven by stricter environmental legislation. Ahead of these regulations, some silicon producers are already substituting carbon reductants by biocarbon [56], in the transition from traditional reducing agents that are also predicted to be scarcer in the future [1]. Other factors such as the costs of production or material scarcity are drivers of the final demand. If we consider an increased flow of waste streams from aluminium and silicon production as well as from downgraded end-of-life materials (e.g. from an overflow of aluminium scrap from end-of-life vehicles), the aluminothermic route could consequently also become cheaper in the future.

Chapter 3

Material and methods

3.1 Life Cycle Assessment methodology

Life cycle assessment is defined by ISO 14040 as: “the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle” [57]. Thus, raw materials and energy inputs and outputs in terms of emissions to the air, water, soil, and wastes, are calculated and their impact aggregated over its life cycle. An LCA consists of four main phases (see Figure 3.1), which are introduced and described for the specific context of the study over this Chapter.

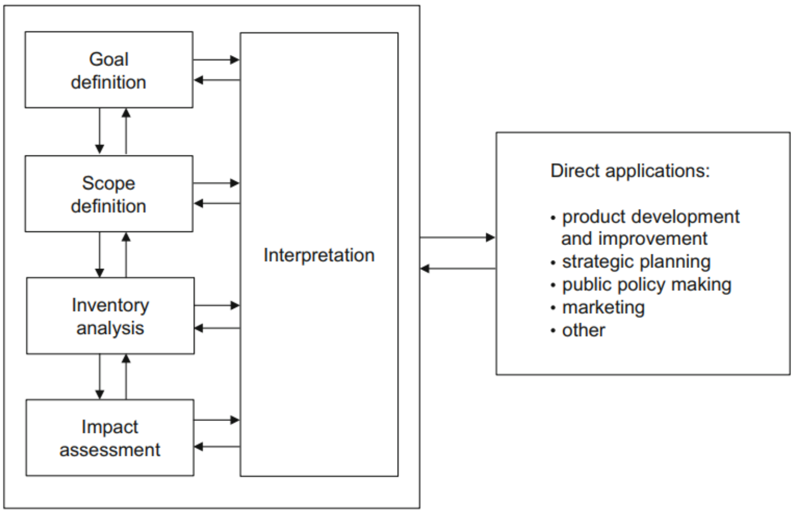

Figure 3.1: Framework of LCA following the International Organization for Standardization (ISO) 14040 standard. The arrows indicate the iterative nature of the LCA procedure, as feedback loops between the different phases may apply. Source: “Life Cycle Assessment: Theory and Practice” [58].

3.2 Goal and Scope definition

In this phase of the assessment, the goal definition establishes the purpose of the study in detail, while the scope determines the systems to be assessed and how this assessment is carried out.

3.2.1 Goal definition

To answer the specific research questions of this study (outlined in Section 1.5), an LCA was carried out. The results of this assessment are intended to benchmark the aluminothermic reduction of silicon and compare it with the conventional production route, looking at different environmental impact categories. Besides, the identification of the main environmental impact contributors in the aluminothermic production is intended to establish potential areas of improvement, a necessary step before structural changes in this industry. This research will support decision making for silicon and aluminium producers, silicon metal consumers, policy-makers, and other potential stakeholders.

3.2.2 Scope definition

Functional unit

The selection of a relevant functional unit (F.U.) allows a fair comparison of the different routes for the production of silicon, acknowledging that the function provided by both systems needs to be equivalent. For instance, it would be a mistake to assume that just by having the same mass of silicon two silicon products fulfil the same function, as these products may display different qualities (summarised in Table 1.1). But the contrary also applies: a functional unit cannot be excessively restrictive because that would only complicate the analysis without adding value, making it more difficult to be used in comparative studies. For instance, in silicon production, metallurgical grade silicon is considered to display purity of around 98-99% Si [59]. It would not add value to choose a specific value within this range since the function that will be addressed is the same.

However, the early stage of development of the SisAl Pilot project means that no experimental data on the final quality of the silicon produced by aluminothermic reduction has been obtained yet. To model this LCA, the functional unit will therefore compare the carbothermic and aluminothermic systems after ladle refining. Theoretically, and according to the mass and energy balances developed, both products will at least achieve the MG-Si quality grade, but early indications show that the aluminothermic silicon could display lower quality than the produced by carbothermic reduction when using aluminium dross as raw material, and that is because it contains certain elements that are not easily removed in the refining process (e.g. Fe, P, Mn...). In the uncertainty analysis (Chapter 4.3), the fact that both products may not display the same quality is assessed.

The functional unit is therefore defined as the production of 1 tonne of silicon after ladle refining. This is the reference flow to which the rest of the flows are scaled. As the silicon concentration is assumed to be similar, both products would therefore deliver equal functionality. As explained later when describing the system boundaries, the production of this F.U. is assessed for Norway.

Type of LCA and handling of multifunctionalities

In this study, both the conventional and aluminothermic production of silicon are multifunctional systems, i.e. they provide more than one function. The conventional production of silicon delivers both metallurgical grade silicon and condensed silica fume. Silica fume, as its name indicates, was previously released through the fumes, but thanks to technological advancements, these particles (mainly consisting of silicon dioxide) are now captured. Its application, especially in the building sector, improves the sustainability and associated greenhouse emissions of cementitious materials [60]. On the other hand, the aluminothermic production of silicon does not produce silica fume as a by-product but a slag containing alumina, which can be further reduced through a hydrometallurgical process for the obtention of this raw material. This hydrometallurgical route is included inside the system boundaries (described later in this Chapter), and therefore this is considered a by-product of the aluminothermic production system, avoiding the processing of raw bauxite to obtain this material. Even if it is not considered a by-product, another function provided by the aluminothermic reduction route is the use of secondary materials that would otherwise end up in waste treatment in an alternative system.

Multifunctionalities can be treated in different ways in an LCA. The ISO 14044 [61] proposes the following hierarchy of solutions:

- Subdivision of unit processes: dividing the unit processes (smallest elements in a life cycle inventory) into two or more sub-processes so each product and by-product has a specific input-output list and impact assigned to it. In our production system, this is not possible since the production of silicon (and the different by-products) is coupled in a chemical reaction and one cannot occur without the other.
- System expansion, or "expanding the product system to include the additional functions related to the co-products" [61]. This is the approach followed by this LCA.
- Allocation: dividing the total inputs and outputs to the process between all the products based on physical causalities (e.g. mass), or economic value, for instance.

The system expansion performed in this study means that when having two different systems the second one is expanded to include the provision of the secondary function of the first system, which is equivalent to credit the first system with the impacts avoided by the alternative production of the secondary function, assuming the most likely alternative way of producing it [58]. Average data for the background system (i.e. processes of the system that are not specific to it in which no direct influence can be exerted by the decision-maker, for example, the electricity supply) were used to achieve representativeness in this substitution. The resulting “expanded system” is represented in Figure 3.2 over the next section. More details on the data acquisition and assumptions will be given during the Inventory Analysis (Section 3.3).

Related to the treatment of multifunctional processes is the modelling framework used in the assessment, which could be attributional or consequential.

The choice between attributional (accounting) LCA and consequential (change-oriented) LCA has a great influence on the results of the assessment. Even though the distinction is not made in the ISO standard, it was recognised in later literature. The following general distinctions between these modelling frameworks can be derived [58, 62]:

- Attributional LCA (ALCA) considers the flows in the environment in a chosen time frame, as a static picture of the system, by using average data. It aims to describe the flows that are relevant for the system studied and answers the question: what environmental impact can be attributed to this product?
- Consequential LCA (CLCA) considers how the flows in the system might change as a response to a perturbation in it, meaning that all the activities that could be affected because of a change in demand for the functional unit are to be included in the analysis. Therefore, the supply chain is dynamic and implies the use of marginal data to account for the smallest changes. For instance, marginal data in electricity generation means that solar or wind energy will not be considered, because they cannot be adjusted to a short-term change in the demand, whether the combustion of natural gas or coal can answer an immediate excess demand. That means marginal data does not assign equal burdens to each unit produced, contrarily to average data. A CLCA, therefore, answers the question: what are the environmental consequences of consuming this product?

For the silicon production system, an attributional LCA would look to the share of global emissions that are attributed to the silicon product studied, without this product affecting the processes in the surroundings. A consequential LCA, on the other hand, would involve studying how the introduction of the aluminothermic production process would affect other activities in the market. For instance, the activities related to the market for silicon skulls, because the utilization of these residues in the aluminothermic production prevents its use in the silicomanganese industry, and consequently, silicomanganese production could decrease. Silicomanganese is a product used during steelmaking that currently has only one substitute: a combination of high-carbon ferromanganese and ferrosilicon [63]. A consequential LCA would therefore include, for instance, increased demand for high-carbon ferromanganese and ferrosilicon. This is just an example of what consequential modelling would involve for the SiSal Pilot project, among many more activities that would be affected in the production system.

As it has been analysed, a CLCA considers physical and monetary causalities, whereas ALCA isolates the system studied from the rest of the world [64]. ALCA, therefore, is generally associated with the use of cut-off in multifunctional processes, whenever the system cannot be subdivided. Contrarily, CLCA is usually associated with the use of system expansion. The International Reference Life Cycle Data system (ILCD) [65], however, recommended a combination of system expansion and attributional modelling for decision-making when the consequences in the background system are limited and do not change significantly the production capacity. In this study, the last approach has been followed. The reason for this is that as the SisAl Pilot would be first only implemented at a Pilot-scale, it does not influence the system at a large scale. Besides, it is considered that the consequences of an aluminothermic production have not been modelled yet to the extent that it is possible to decide on reasonable assumptions that a consequential approach would draw to the system. It is preferred that the simulation is feasible and accurate to the extent that existing data allows, rather than more uncertain and very comprehensive modelling.

The long-standing debate between attributional and consequential LCA and handling of multifunctionalities is still ongoing, as some authors consider that attributional LCAs should not use system expansion, while others question the validity of system expansion itself [66]. Of a different opinion are other studies that argue that all LCAs are intended to take some kind of decision and therefore should be consequential [e.g. 67]. Current practices indicate that most of the LCAs performed are, however, attributional, and 31% of attributional studies also use system expansion as a way to handle multifunctionality [66]. Recent trends are seeing a rise in the studies considering both attributional and consequential analysis as a way to complement each other, since the questions they respond are different [66, 68]. Future analysis of the SisAl process may consider the application of consequential LCA once the influence of the aluminothermic process in the system is better studied, and to examine the implementation of this process at a larger scale.

System boundaries and limitations

The system boundaries of an LCA differentiate the analysed processes from the surrounding economic system (technosphere) and environment (ecosphere) and define the unit processes included in the assessment.

In this study, a “cradle-to-gate” approach is taken, meaning that the upstream emissions of the production of silicon are included (i.e. from the extraction of raw materials to the actual production of the F.U.), but not considering the impact after the silicon has acquired the desired quality, and excluding further processing, transportation, use and end-of-life (downstream activities).

The rationale behind this decision lies in that the life-cycle processes that the product undergoes after the obtention of silicon are the same for both production routes, which was also accounted for in the definition of the functional unit. This disregards that the transportation distances of the final product may be greater in the carbothermic route when looking to Europe, as the EU is still a net importer of silicon metal [9]. In contrast, the aluminothermic route would require lower transportation distances as the project would be mostly implemented locally rather than in third countries from outside Europe (involving silicon and aluminium producers, waste-handlers and research institutions from Norway, France, Greece, Germany, Spain, Iceland or Italy) [69]. However, downstream transportation distances are overlooked in this assessment both because this data is not available yet as the project is on a pilot phase and because it cannot be assumed that the consumption of this product will remain within Europe and not be exported.

Other limitations of the study are found in the assumptions taken. For instance, only some raw materials have been considered inputs for the aluminothermic reduction (i.e. silicon skulls and aluminium dross) while other types of silicon and aluminium raw materials could have been evaluated. As the project is on a pilot phase, just certain chemical characterization analyses have been carried out and that has limited the scope of the present study. When data on specific raw materials and emission factors were not available, these were assumed to be an average (these assumptions are made explicit when analysing the inventory in Section 3.3). Besides, other assumptions have been taken regarding the background data, as information is not available on the emissions and wastes produced from the raw material providers in the different silicon production routes, the background processes have been extracted from ecoinvent which at the same time assumes an average of the sector considering current technologies.

Finally, the system boundaries considered in this study are depicted in Figure 3.2. Note that the production of raw materials upstream is included, and also the obtention of the by-products for both systems (silica fume in the carbothermic silicon production and alumina in the aluminothermic silicon production route). As it has been mentioned before, the alumina contained in the slag is separated through alkaline leaching, and therefore this process is also included within the system boundaries.

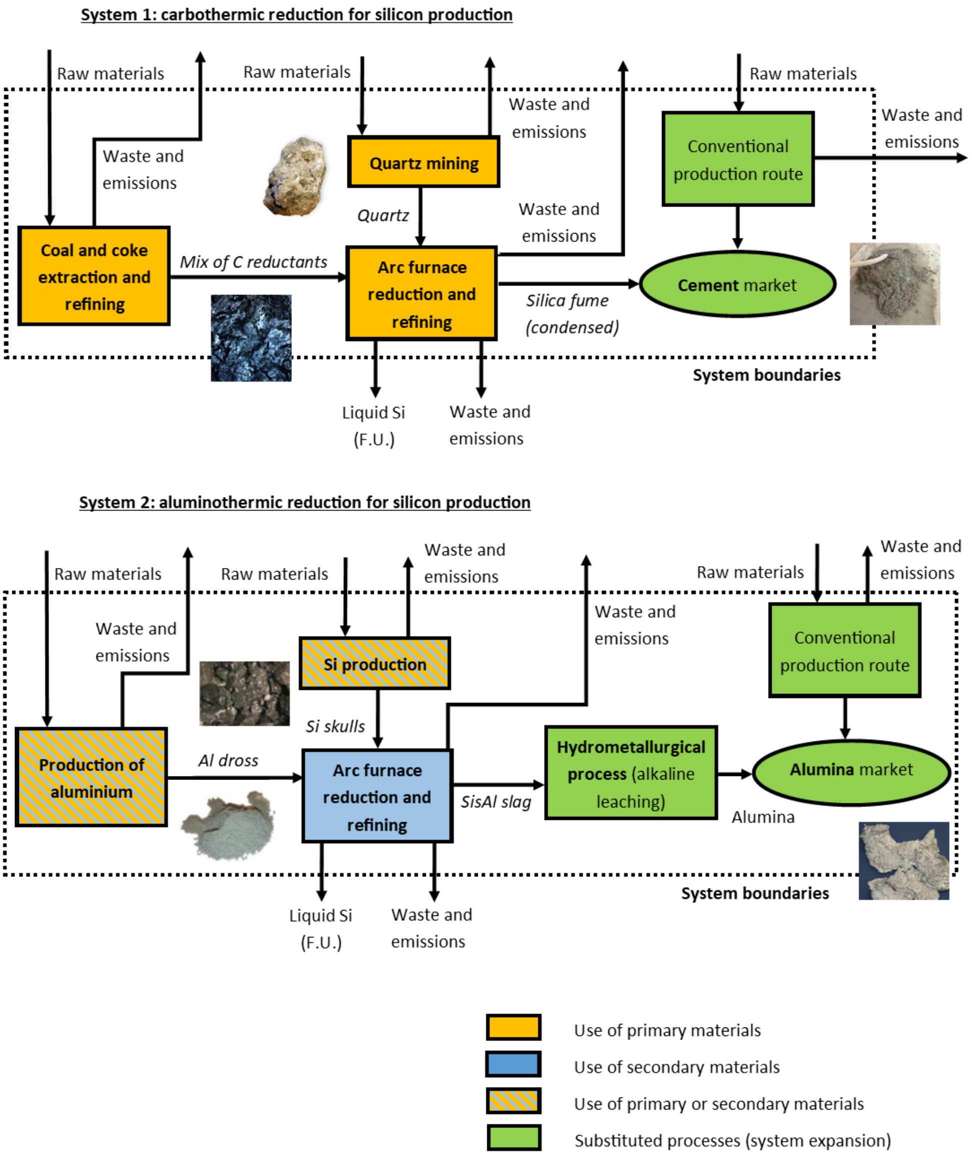

Figure 3.2: Expanded system flowcharts. The by-products with economic value have been included inside the system boundaries. The photographs represent the main inputs and outputs that vary between both systems. Source: silicon skulls and aluminium dross pictures (SisAl Pilot Consortium); quartz, coal, concrete and alumina images from Wikimedia Commons.

It is important to mention that the geographical boundaries of this LCA consider the production of silicon in Norway, as the data on raw materials have been gathered from companies of the SisAl Consortium set in Norway. Besides, this geographical location is considered especially relevant since Norway is the largest provider of the EU supply regarding silicon metal (see Figure 3.3).

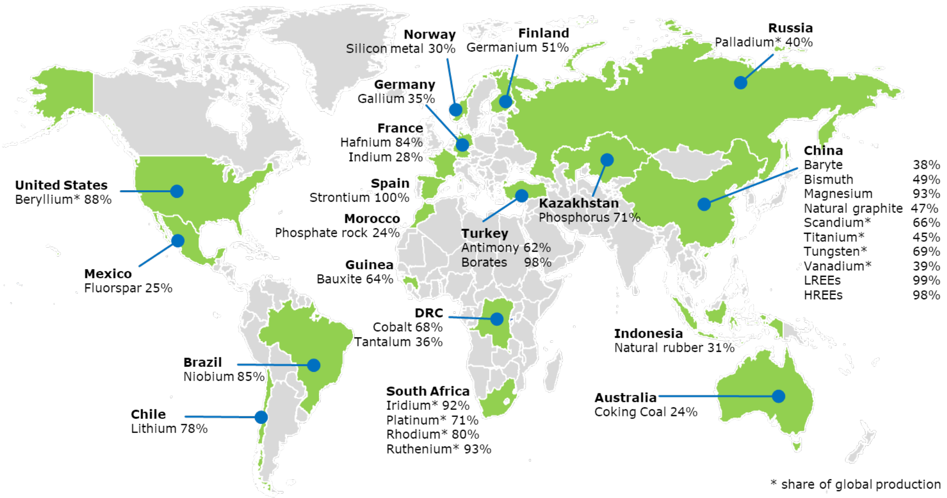

Figure 3.3: Countries accounting for the largest share of EU supply of CRMs. Source: European Commission [70].

Data quality requirements

Data for the foreground system and background system need to represent time, level of technology and geographic coverage in accordance with the system boundaries across the different production routes.

To this end, and as is further developed during the Inventory analysis (Chapter 3.3), data for the foreground system is constructed from characterization of raw materials and process modelling of companies participating in the SisAl Pilot. When the use of first-hand data was not possible (e.g. for emissions related to impurities in the raw materials that were not accounted for in the mass and energy balances) emission factors have been used, representing when possible an average of the sector in Norway, while other materials generally imported to Norway were assigned a European average.

Regarding background data, this is not usually in possession of the industry and therefore it was taken from ecoinvent.

To develop the Life Cycle Inventory (LCI) and Life Cycle Impact Assessment (LCIA) results, emission factors and characterization factors are needed. Even though the LCI and LCIA are explained further below (Chapters 3.3 and 3.4, respectively), these concepts are introduced now to be able to discuss their quality requirements.

An emission factor is "a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated to the release of that pollutant" [71]. Emission factors, therefore, define the average levels of emissions per activity produced. In this study, emission factors are used to account for some of the emissions in the Submerged Arc Furnace. Emission factors should not be mistaken with characterization factors or “scientifically based indicators that are quantitative measures of environmental impact” [72]. To mention a broadly used example, the indicator that relates the emissions of CO_2 with the global warming impact category (1 kg CO_2 = 1 kg $CO_{2\ \mathrm{eq.}}$), is a characterization factor. CO_2 equivalent is the unit for measurement of the potential global warming impact for any elementary flow. Other GHGs display a different global warming impact, but they are always measured in comparison to CO_2 (e.g. CH_4 = 28 kg $CO_{2\ \mathrm{eq.}}$, N_2O = 265 kg $CO_{2\ \mathrm{eq.}}$, etc. [73]).

The characterization and emission factors considered in this study belong to ecoinvent and literature sources, respectively, both of which display recent available data. The version of ecoinvent used for this study (ecoinvent 3.5) uses data that has not been updated since 2018, and the literature sources used vary in their publication date, but these were the most up-to-date and available sources of information found. There is always some inherent uncertainty in the use of old data, even if it is quite recent. However, to be able to study this uncertainty, the sources of information are disclosed and discussed qualitatively (in Chapter 4.3). Furthermore, it is recommended that this study is repeated in the future to reflect the change in emission and characterization factors and account for the variation on the impact that this may cause.

The inventory and assumptions taken are further developed in Section 3.3.

Impact categories, method and software tools

This study uses the impact method ReCiPe 2016 (H) to evaluate impact at the Midpoint and Endpoint levels. H stands for Hierarchist approach, which applies a balanced weight between short and long term perspectives [58], and is often considered to be the default model in scientific research [74]. Besides, some of the advantages of using the ReCiPe impact method is that it includes the most complete set of midpoint impact categories and it applies a global scope [74].

In the software SimaPro, elementary flows (resources used, emissions and other wastes) are first classified into the different impact categories to which they contribute. Then, through characterization factors, these emissions and resource extractions are translated and aggregated into the associated potential environmental impacts, as shown in the equation below (Equation 3.1).

$$LCIA_j = \sum_i LCI_i \times CF_{i,j} \tag{3.1}$$

where:

$LCIA_j$ = life cycle impact assessment result (for an impact category).

LCI_i = sum of a specific elementary flow throughout the inventory.

$CF_{i,j}$ = characterization factor that relates an specific elementary flow to an impact category.

Note that i takes the values of all the elementary flows in the inventory. Equation 3.1 is based on the ecoinvent formula [75].

Characterization factors at the midpoint level group these impacts into single environmental problems (see Figure 3.4 below). Endpoint indicators, however, display the impact on higher aggregation levels (Areas of Protection), but the associated uncertainty consequently increases.

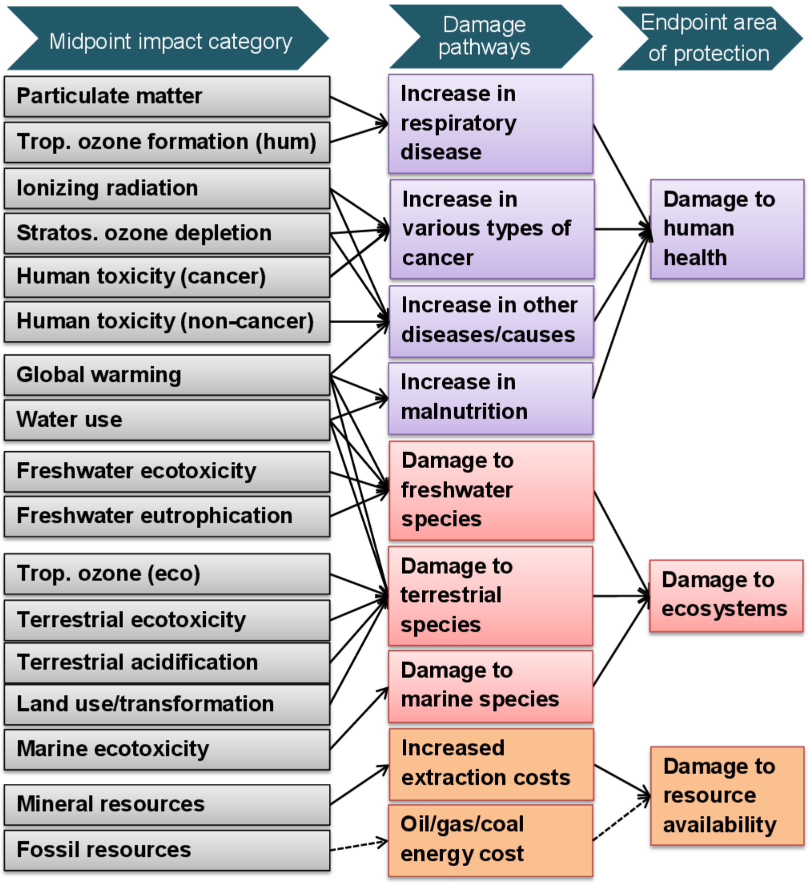

Figure 3.4: Overview of the structure and impact categories of ReCiPe 2016. Source: “ReCiPe 2016: a harmonised life cycle impact assessment method at midpoint and endpoint level” [76].

Endpoints provide information that is condensed into fewer impact categories, which also makes them easier to be interpreted, as they display Areas of Protection (AoP), and represent the damages that humans value the most. For example, society cares about climate change, as global warming affects both human health and ecosystems. The ultimate goal of avoiding climate change is the protection of these endpoints, rather than global warming as such. On the other hand, when analysing endpoints the details on the damage pathways are lost. The assessment of both midpoint and endpoint impact levels, therefore, supports the interpretation of the results by complementing each other [58].

Characterization factors at the endpoint level are derived from the characterization factors at the midpoint level, by applying a midpoint to endpoint factor that is constant for each midpoint impact category [76].

The selection of relevant impact categories is an essential step of the Life Cycle Impact Assessment. Based on what previous studies identified to be the most impactful categories for the silicon and aluminium industries (in Chapter 2), and a preliminary assessment in the different emission of pollutants between the carbothermic and aluminothermic routes (see Chapter 1.4), the following midpoint impact categories will be analysed in this study: global warming, ozone formation, fine particulate matter formation, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, marine ecotoxicity, human carcinogenic and non-carcinogenic toxicities, land use, mineral resource scarcity and fossil resource scarcity.

Some categories overlooked in this assessment include water scarcity, which is left out of the study because Norway currently does not bear high water stress [77], as well as the ionizing radiation and ozone depletion potential since there was not a significant variation detected in the release of pollutants associated with these categories.

A brief introduction to the studied impact categories is displayed below. This description is based on the one given at ReCiPe [76] and "The hitch hiker's guide to LCA: an orientation in life cycle assessment methodology and application" [72].

Global warming. Global Warming Potential (GWP) expresses the radiative forcing capacity of a GHG i.e. the capacity to absorb infrared radiation and therefore heat the atmosphere. When applying the hierarchist view, as in this study, the additional radiative forcing is integrated over 100 years. GWP is measured in kg $CO_{2\ eq.}$. Global warming is associated with the endpoints in the ReCiPe methodology for human health and damage to ecosystems.

Toxicity (carcinogenic, non-carcinogenic, freshwater, terrestrial and marine). Toxicity potentials depend on the fate and exposure as well as on the toxicity of a chemical, including many substances and also different impacts. The Toxicity Potential (TP) is expressed in kg 1,4-dichlorobenzene-equivalents (1,4 $DCB_{eq.}$), which is a known pesticide. The endpoint characterization factors correspond to human health and damage to ecosystems.

Particulate matter. Measured in kg $PM_{2,5}$ equivalent. Fine particulate matter with a diameter lower than 2,5 μm causes human health problems as it can reach the upper part of the airways and lungs. The emissions of particulate matter are therefore related to human health impacts.

Terrestrial acidification. The acidification capacity of a pollutant is defined as the number of H^+ ions produced per mass of substance and is measured as the potential soil acidity that a substance can enhance relative to SO_2. This parameter reflects the maximum acidification capacity of a substance, which nevertheless would vary depending on where the acidifying emissions are deposited (e.g. the buffering capacity of the soil). A change in the acidity of the soil is harmful to plant species, causing damage to ecosystems.

Ozone formation (human and ecosystems). Ozone is formed through a series of photochemical reactions of NOx and Non-Methane Volatile Organic Compounds (NMVOCs). Ozone is the cause of health problems such as irritation to respiratory systems, but it can also have impacts on vegetation. This impact category is measured in NOx equivalent. The associated endpoints are damages to human health and ecosystems.

Freshwater and marine eutrophication. Eutrophication is caused by excessive levels of nutrients leading to increased biological production and oxygen consumption, therefore resulting in detrimental impacts on aquatic ecosystems. Freshwater eutrophication is measured in kg P equivalent and marine eutrophication in kg N equivalent, according to the limiting factor in each aquatic ecosystem.

Land-use. Land-use covers the use and transformation of land, as well as changes in biodiversity and support functions, in comparison with a reference state (in the ReCiPe methodology, the potential natural vegetation, or mature vegetation that would develop without the influence of new human activities). The midpoint characterization factor is measured in annual crop equivalents. This impact category is, however, difficult to assess due to lack of knowledge, and also debated concerning if it should be classified as a resource use problem. Currently, the final endpoint for this midpoint impact category in ReCiPe is only damage to ecosystems.

Mineral resources. Mineral resource extraction will cause a decrease in the ore grade. This is combined with the expected future extraction of a mineral resource, leading to the midpoint characterization factor or Surplus Ore Potential (SOP), which expresses the extra amount of ore that is to be produced in the future as a consequence of the extraction of 1 kg of a mineral resource, relative to the extra amount of ore produced due to the extraction of 1 kg of copper in the future. Therefore, it is measured in kg Cu equivalent. The endpoint affected is damage to resource availability.

Fossil resources. The midpoint indicator for this last category is the ratio between the energy content of the fossil resource and that of crude oil, expressed as kg oil equivalent. As in mineral resources, the endpoint affected is also damage to resource availability.

It is worth noting that some elementary flows are classified into more than one environmental impact category. That is the case of, for instance, NOx that can lead to photo-oxidants formation, then cause the release of H^+ acidifying emissions, and later contribute to acidification through the nitrogen atom [72]. This is only possible if the effects are independent of each other. If they are dependent only the primary effects are accounted, to avoid double-counting.

3.3 Inventory analysis

3.3.1 Foreground modelling

The life cycle of any product usually covers many different activities, accounting for both the foreground and background systems. Therefore, it is common practice to collect the data available in the foreground system while modelling the background data as generic information from an LCI database.

In the Life Cycle Inventory, the inputs and outputs considered to deliver the functional unit to both the carbothermic and aluminothermic reduction are developed, compiling flows of inputs (materials or other resources) and outputs (emissions, waste, products and by-products). The LCA foreground inventory for this study is constructed from:

- **Thermodynamic process simulations and mass and energy balances** developed in HSC Chemistry and provided by Alejandro Abadías Llamas, from the Helmholtz Institute Freiberg for Resource Technology (HZDR), a research organisation and partner in the SisAl Pilot[1]. The modelling is still ongoing, but this study considers the latest results available, using the characterised materials from different companies in the SisAl pilot (composition for silicon skulls, aluminium dross or the reductants in the conventional reduction process[2]). The yield is assumed to be 90% for the carbothermic reduction, as found in the literature [e.g. 21].
- **Emission factors**, for some other pollutants that were not included in the mass and energy balances, because the model considered a high purity of the reductants used. The emission factors in this study allow to account for CH_4, NOx, dioxins, PAHs, PM_{10} and $PM_{2,5}$ in the carbothermic route (see emission factors in Table B.1 in Appendix B).
- **Estimations** for other emissions in the aluminothermic route, as the carbon reductants are not present in this process those emissions related to

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[1] Data received from Alejandro Abadías Llamas (HZDR). SAF and SisAl modelling on March 2 2021. SisAl modelling including hydrometallurgical purification of alumina on April 19 2021.

[2] Composition given by the SisAl Consortium.

the combustion are minimal. NOx is estimated to be a 10% of the release in the carbothermic reduction, and the emissions of PAH and SO_2 are considered negligible[3], Besides, $PM_{2,5}$ is estimated to account for less than 3 microgrammes per cubic metre in the off-gas, while the emissions of PM_{10} are also negligible[4]. Dioxins are considered minimal in this process as they are released from organic materials.

- **Trace elements composition** to account for the emissions of metal oxides in the carbothermic route. The trace metals content in raw materials is retrieved from literature [78, 79] and displayed in Table B.2 in Appendix B. Mercury (Hg), sulfur (S), arsenic (As) and selenium (Se) are the elements that are mostly present in the filtered off-gas [78], partly due to their low boiling temperature in comparison with the process temperature (estimated to be at 2000ºC in the conventional reduction [17] and between 1500-1600ºC in the SisAl pilot [27]). As trace metals get distributed between the Si-metal, micro-silica and off-gas phases, a partition coefficient is applied (see Table B.3 in Appendix B). Sulfur is assumed to be completely oxidized when leaving the furnace, as it will enter in contact with oxygen. These calculations are not developed for the aluminothermic route since trace metal emissions were already included in the thermodynamic process simulations.
- **Ultimate analysis** of woodchips, to determine the relevance of the contribution of this reductant material to biogenic emissions. As the emissions released in the combustion of woodchips are generated from the carbon contained in the biomass, which was absorbed while the plants grew, the carbon and emissions associated were already part of the biogenic cycle and therefore its release is accounted as neutral, contrary to fossil emissions (e.g. from hard coal) that have remained locked in soils for millions of years. Fossil and biogenic emissions would contribute equally to global warming in terms of GWP, but biogenic emissions account as “zero” impacts just for modelling purposes. To calculate the release of biogenic emissions the woodchips used are extracted from the inventory and multiplied by their total carbon content (in Table B.4) in Appendix B, then the carbon content is converted to CO_2 emissions through their molar mass ratio (44/12).

The complete inventory can be found over the next pages (Tables 3.1 and 3.2).

In the inventory, it is appreciated that allocation at Point of Substitution (APOS) has been used to include a system expansion approach to handle multifunctional products. Different colours represent the results from mass and energy balances in HSC received from HZDR (not coloured), the pollutants included in the inventory through emission factors and other estimations (in blue) and the elements estimated using data from trace elements and ultimate analysis (in orange).

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[3] Torstein Haarberg, exploitation manager (personal communication, November 3, 2020).

[4] Gabriella Tranell, project coordinator (personal communication, November 24, 2020).

To refer to specific flows detailed in the inventory, the flowcharts showing the different inputs and outputs for both the carbothermic and aluminothermic reduction processes are shown in Appendix C. Note that all intermediate inputs and outputs are displayed, but these are balanced in the inventory so only the flows that cross the system boundaries are accounted for.

Table 3.1: Inventory for the carbothermic reduction in SimaPro per F.U.

Input / Output	**Amount**	**Comment**
	Outputs to technosphere: Products and co-products	
Carbothermic Si	1 t	The F.U. of this system. Produced by carbothermic reduction.
	Outputs to technosphere. Avoided products	
Silica sand (GLO) | market for | APOS, U	0,27 t	The by-product of silicon conventional production, applied in buidings. In the form of fine particles.
	Inputs from nature	
Water, process, unspecified natural origin/kg	17,57 t	Water to pump, employed in the heat recovery boiler.
Air	83,2 t	To provide the necessary oxygen for the main reaction occuring in the furnace (Equation 1.1) and in the refining process at the ladle.
	Inputs from technosphere: materials/fuels	
Silica sand (GLO) | market for | APOS, U	2,68 t	Note that this silica sand is in the form of quartz, contrary to the recovered silica fume (by-product of silicon production), which is recovered as fine particles.
Wood chips, wet, measured as dry mass (Europe without Switzerland) | market for | APOS, U	0,47 t	Carbon reductant used in the conventional production, in this study it is assumed a typical composition of 35% of this reductant feed (data provided by the SisAl Consortium).

Hard coal (Europe, without Russia and Turkey) | market for hard coal | APOS, U	1,65 t	Assumed to be 65% of the total reductant feed (data provided by the SisAl Consortium).
Quicklime, in pieces, loose (RoW) | market for quicklime, in pieces, loose | APOS, U	0,04 t	Applied in the refining ladle process.
Inputs from technosphere: electricity/heat		
Electricity, medium voltage (NO) | market for | APOS, U	13.474,08 kWh	Consumed in the SAF process and in the pump.
Emissions to air		
Carbon dioxide	4,96 t	Determined by mass and energy balance in HSC. This number does not include biogenic emissions.
Carbon dioxide, biogenic	0,85 t	These emissions of CO_2 come from the combustion of woodchips, and therefore are considered biogenic. Calculated from first principle (i.e. through total mass of woodchips, the carbon content in woodchips (in Table B.4), and molar mass relation between carbon and CO_2).
Water, NO	20,04 t	Determined by mass and energy balance in HSC.
Heat, waste	2.524,24 t	Determined by mass and energy balance in HSC.
Nitrogen oxides	22 kg	Calculated through emission factors in Table B.1.
Methane	1,2 kg	Calculated through emission factors in Table B.1.
Dioxins (unspec.)	3 μg	Calculated through emission factors in Table B.1.

PAH, polycyclic aromatic hydrocarbons	3 g	Calculated through emission factors in Table B.1
Particulates, $< 2{,}5\ \mu m$	600 g	Calculated through emission factors in Table B.1.
Particulates, $< 10\ \mu m$	850 g	Calculated through emission factors in Table B.1.
Mercury	14,83 mg	Estimated using data from elemental analysis (Tables B.2 and B.3).
Sulfur dioxide	20,02 kg	Estimated using data from elemental analysis (Tables B.2 and B.3).
Arsenic	91,84 mg	Estimated using data from elemental analysis (Tables B.2 and B.3).
Selenium	447,76 mg	Estimated using data from elemental analysis (Tables B.2 and B.3).
	Outputs to technosphere: Waste treatment	
Slag from metallurgical grade silicon production (GLO) | market for | APOS, U	0,23 t	Slag obtained from the production of silicon.

Table 3.2: Inventory for the aluminothermic reduction in SimaPro per F.U.

Input / Output	Amount	Comment
Outputs to technosphere: Products and co-products		
Aluminothermic Si	1 t	The F.U. of this system. Produced by aluminothermic reduction.
Outputs to technosphere. Avoided products		
Aluminium oxide (GLO) | market for | APOS, U	0,9 t	The by-product of aluminothermic silicon production, after refining the process slag.
Inputs from nature		
Water, process, unspecified natural origin/kg	0,48 t	Na_2CO_3 solution, where this compound is recirculated in the process and therefore only water is needed as an input.
Air	4,16 t	Cooling air in the alkaline route.
Inputs from technosphere: materials/fuels		
Silica sand (GLO) | market for | APOS, U	2,58 t	In the model, silicon skulls are used rather than silica sand as a source for Si. However, this by-product from silicon production is not defined in ecoinvent 3.5, where all the residues from metallurgical-grade silicon production are considered to be contained in the slag. Since silicon skulls hold economic value for the Si-Mn industry, this flow is instead replaced by the raw material that would feed the Si-Mn industry in the first place, if silicon skulls were not used. However, this holds a greater impact discussed during the uncertainty analysis (Section 4.3).

Aluminium oxide (GLO) | market for | APOS, U	0,3 t	A by-product from the producing companies, it is added to reach a higher concentration of Al during the slag conditioning. This by-product is not pure aluminium oxide, since it contains some other substances, being this its major compound. An overestimation of the impact can be derived by the use of this flow, which is produced through the Bayer process, and this uncertainty is assessed during the uncertainty analysis (in Section 4.3).
Petroleum coke (GLO) | market for | APOS, U	6,66E-02 t	Fuel calcined in the alkaline route.
Quicklime, in pieces, loose (RoW) | market for quicklime, in pieces, loose | APOS, U	2,71 t	Applied in the slag making, conditioning and hydrometallurgical obtention of the alumina route.
Carbon dioxide, liquid (RER) | production | APOS, U	1,58 t	CO_2 is used in the carbonation process belonging to the alkaline route.
Inputs from technosphere: electricity/heat		
Electricity, medium voltage (NO) | market for | APOS, U	6.972,69 kWh	For the slag-making, aluminothermic reduction and slag conditioning and in the alkaline leaching route.
Emissions to air		
Carbon dioxide	0,24 t	Determined by mass and energy balance in HSC.
Water, NO	0,48 t	Determined by mass and energy balance in HSC.

Nitrogen oxides	2,2 kg	Estimated to be a 10% of the released in the carbothermic production (see explanation above in Section 3.3.1.)
Particulates, < 2,5 μm	9,99 mg	Estimated from concentration in the air released (see explanation above in Section 3.3.1.)
Outputs to technosphere: Waste treatment		
Dross from Al electrolysis (GLO) | market for inert waste | APOS, U	-0,87 t	Dross is used as a raw material for the aluminothermic production and is therefore considered as a negative output (input) to this process because it is being removed from the technosphere.
Inert waste (Europe without Switzerland) | market for | APOS, U	2,31 t	The sum of the residue from $CaO{\cdot}SiO_2$ separation and the SisAl refining slag, which are considered to be inert and go to inert deposit.
Hazardous waste, for underground deposit (GLO) | market for | APOS, U	4,26 t	Precipitates that are produced in the hydrometallurgical route for the obtention of alumina, during the $CaCO_3$ separation. As the experimental analyses have not taken place yet, a worst-case scenario in which these residues are hazardous is considered, to not overestimate the positive contribution of the aluminothermic process.

3.3.2 Background modelling

The background system makes up to 99% of the unit processes in a product's system [80]. In this study, to model the background system the comprehensive and widely used ecoinvent database is chosen. Ecoinvent gathers LCI data that is transparent and reliable, making it possible to perform LCA studies and increasing the credibility of results. This comprehensive dataset displays background data for unit processes with global coverage, as well as data representing specific geographies.

The processes in this database represent in most cases an average of the sector in a specific location, making it suitable to model the background of our system, as data for the providers is generally not known.

A unit process is represented in the database as direct inputs and outputs of unit processes, which at the same time are built from inputs and outputs of more unit processes, ideally until all the inputs and outputs are elementary flows from and to the ecosphere (resources and emissions), in an interlinked unit process supply chain. The individual datasets of unit processes in the transformation level are then linked through the market datasets, which account for the consumption mix of a product.

There is not a strict cut-off rule in this database. Therefore, datasets are as complete as there is knowledge available [81].

3.4 Impact assessment

In this last phase of the LCA methodology, the flows of materials and energy per functional unit of product are expressed in terms of environmental impact, in the impact categories defined in the Scope of the study (see Section 3.2.2).

The characterization factors (CF) of the ReCiPe 2016 (H) methodology both at the midpoint and endpoint levels are accessible through ecoinvent. In SimaPro, these CF are linked to their specific elementary flows and therefore assigned to the inventory. LCIA results are calculated for both the carbothermic and aluminothermic routes in SimaPro, combining the inventory for the background and foreground processes. The results of this assessment are described later in Chapter 4.

3.5 Interpretation

Defined in the ISO 14040 [57] as the "phase of life cycle assessment in which the findings of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goal and scope in order to reach conclusions and recommendations", it supports the iterative approach of the LCA (feedback loops in Figure 3.1).

Hauschild et. al [58] describes that the first step of the interpretation phase is the identification of significant issues (i.e. those with the potential to change the final results of the assessment, e.g. methodological choices, assumptions, inventory data...) using tools such as sensitivity analysis. Then, the significant issues are evaluated in terms of completeness, reliability and consistency, improving them when necessary, which will affect previous phases of the LCA. Finally, the conclusions and recommendations of the study are drawn, considering the limitations identified in earlier phases. Preliminary conclusions can also lead to a change in the scope definition if the conclusions drawn are not aligned with the requirements of the study.

Therefore, the interpretation in this study was developed throughout all the previous phases of the LCA (Goal and Scope definition, Inventory analysis and Impact Assessment), and feedback loops were applied, for example, when validation rounds took place within the different stakeholders in the SisAl pilot Consortium, to improve the data quality and assumptions taken throughout the study.

The interpretation of the results obtained for the environmental impact attributed to the midpoint and endpoint categories, as well as uncertainty and sensitivity analysis and scenario evaluation is carried out in the next section (Chapter 4).

Chapter 4

Results and discussion

Once the Goal and Scope had been defined (in Chapter 3.2), and the LCI was performed (in Chapter 3.3) the impact assessment took place. The main results of the LCIA, considering the limitations and assumptions described are displayed below in Figure 4.1. These results evaluate the contribution to the environmental impact of the production of 1 tonne of silicon after refining in Norway, following the carbothermic and aluminothermic production routes.

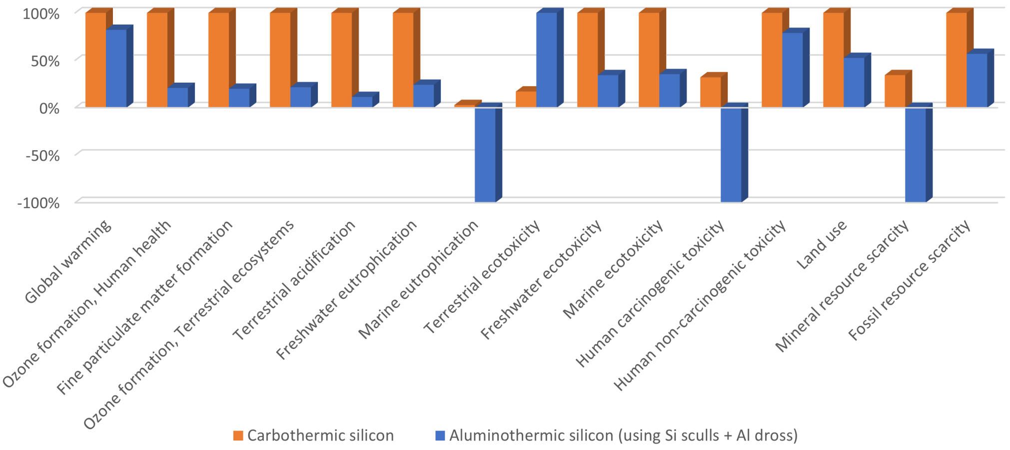

Figure 4.1: Comparison of the overall midpoint impact results for the carbothermic and aluminothermic systems. F.U.: 1 tonne of silicon after ladle refining in Norway.

In Figure 4.1 the differences in the impact for the production of 1 tonne of Si for various impact categories are observed. An overall decrease of the impact for most impact categories can be appreciated. The contribution of the aluminothermic production route to global warming, when using Si skulls and Al dross as inputs for this process, accounts for around four-fifths of the impact when compared to the carbothermic route. Most impact categories show an even greater decrease, sometimes reaching negative contributions (positive impact on the environment, as the production of the alumina by-product avoids more impact than the impact produced in the silicon production process itself). That is the case for the following impact categories: marine eutrophication, human carcinogenic toxicity and mineral resource scarcity. On the other hand, from the impact categories studied only the terrestrial ecotoxicity impact hold a higher contribution when applying the aluminothermic reduction than in the carbothermic route.

To study the contribution of the different unit processes and emissions/wastes generated in both systems for silicon production, a hotspot analysis is developed. The main contributors affecting each impact category are analysed and explained below.

4.1 Contribution analysis

4.1.1 Global Warming

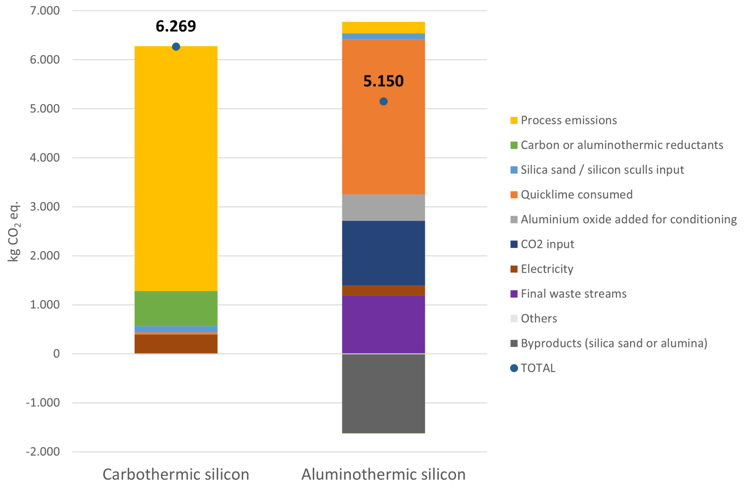

Figure 4.2: Comparison of the global warming impact for the aluminothermic and carbothermic processes. Expressed in kg $CO_{2\ eq.}$. F.U.: 1 tonne of silicon after ladle refining in Norway.

In Figure 4.2 the carbothermic and aluminothermic silicon production routes are compared in terms of their contribution to the **global warming impact**. In the graph, the result of the addition of the impacts associated with each of the unit processes belonging to a production system is represented by a blue dot. Due to the impact avoided by the production of secondary products (and the utilization of secondary raw materials), it can be observed that the overall impact score decreases in both routes. However, the avoided emissions are substantially higher in the aluminothermic silicon production route, as alumina production involve larger emissions of GHGs, than the production of silica sand.

When looking at the greater contributors to the global warming impact, the emissions from the furnace in the carbothermic route stand out (approx. 80% of the contribution). This is due to most of the GHGs being released from the reactions occurring in the furnace (including the emissions of e.g. CO_2, water vapour, NOx, or CH_4). The majority of the remaining global warming impact in the carbothermic route is caused by the use of carbon reductants and the electricity consumed.

On the other hand, in the aluminothermic route, the emissions from the process itself account for less than 5% of the impact, while the most impactful emissions for this production route are found in the calcium oxide consumed in this process (almost 50% of the global warming impact). The reason behind this high contribution is found in the production of CaO (commonly known as quicklime or burnt lime) from limestone ($CaCO_3$) which releases large quantities of CO_2 emissions. The second highest contributor to global warming for the aluminothermic production system is the input of carbon dioxide (used in the hydrometallurgical process). The production of industrial carbon dioxide for commercial use also releases carbon dioxide (together with methane and other GHGs), as the commercial CO_2 production is normally a by-product of ammonia and hydrogen production, but this process releases much more carbon dioxide than it is recovered [82]. The flow of hazardous waste also accounts for almost a fifth of the impact score to this category. As these residues need underground containment, the impact associated with the steel production for the underground container is allocated to this waste management process. The remaining environmental impact for this impact category following the aluminothermic route is associated with the production of aluminium oxide (around 8%), and with other unit processes to a minor extent.

4.1.2 Ozone and fine particulate matter formation

In Figure 4.3 (in the next page) the **ozone formation impact** is represented (left graph). These numbers account for the potential impact on human health and terrestrial ecosystems caused by ozone formation in the carbothermic and aluminothermic systems. Human health and terrestrial ecosystems impacts regarding ozone formation look overall the same since they are affected similarly by the elementary flows studied and therefore are represented in just one graph and commented as a whole.

The emissions from the furnace account for more than 80% of the impact regarding ozone formation in the carbothermic route. This is mostly due to pollutants such as NOx. The second unit process accounting with the highest contribution to ozone formation in the carbothermic route is found in the carbon reductants used, and this is observed to be linked to the emissions in the transport and mining and operation of mainly hard coal, as woodchips account with a minimal impact in this category. The rest of the unit processes in the carbothermic system do not hold a significant impact on this impact category.

On the other hand, the impact associated with the aluminothermic route is found to be much more homogenous, with the ozone formation impact distributed more equally between the different unit processes. The final waste streams pose the highest contribution to this impact category, and this is again caused by the emissions in the production of the steel for the underground containment of hazardous wastes. The alumina by-product decreases substantially the impact of ozone formation in terrestrial ecosystems and human health ozone formation.

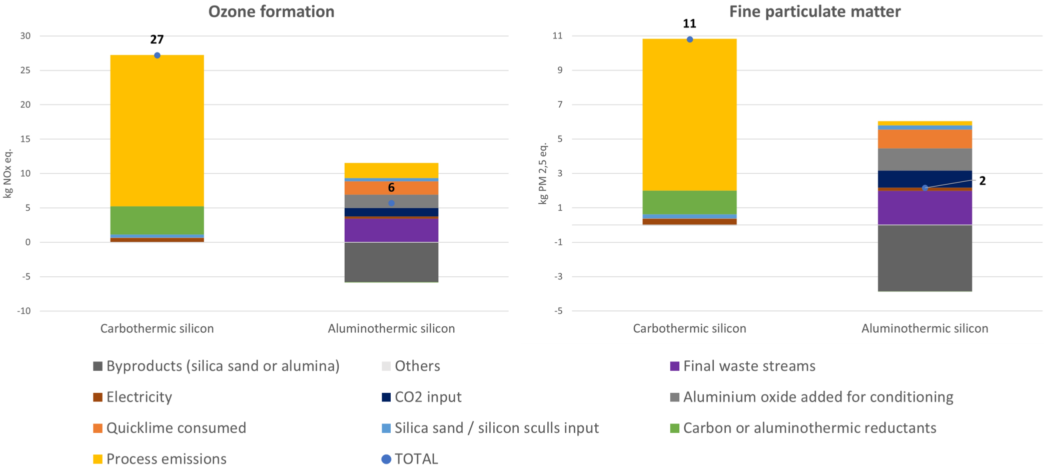

Figure 4.3: Comparison of the ozone and particulate formation impacts for the aluminothermic and carbothermic processes. Expressed in kg $NOx_{eq.}$ and kg $PM_{2,5\ eq.}$, respectively. F.U.: 1 tonne of silicon after ladle refining in Norway.

Regarding **fine particulate matter formation impact** (in Figure 4.3, right graph) the carbothermic silicon route scores higher for this category. This impact is mainly attributed to the emissions in the process, as it has been commented before the conventional production of silicon releases dust in the form of $PM_{2,5}$ and PM_{10}. The carbon reductants input is the second-highest contributor, an impact that is especially associated with the use of hard coal, which releases particulate matter in various stages of its life cycle such as in the blasting process but also due to the emissions associated with its transportation. The rest of unit processes account for a small share of the impact in this production route.

When analysing the aluminothermic route, the impact is mostly associated with the final waste streams (impact connected with the production of pig iron for the construction of the underground container), the aluminium oxide used, the quicklime consumed and the input of carbon dioxide. These industrial processes account for a large release of particulate materials in the background system.

However, this impact is lower than the associated with the carbothermic route and gets largely compensated by the emissions avoided in the production of alumina.

4.1.3 Freshwater and marine eutrophication

In Figure 4.4 (left graph) the contribution of the carbothermic and aluminothermic route to the **freshwater eutrophication impact** category is displayed. It can be observed that the carbothermic route holds a lower performance for this impact category, as its impact is higher. The freshwater eutrophication impact in the carbothermic route is more than 90% associated with the input of hard coal. Especially in the mining of hard coal, the emissions due to the leaching of the spoil (or waste material removed during mining) contribute strongly to this impact category, as a large amount of phosphates and other eutrophication drivers are emitted.

In the aluminothermic system, these emissions occur in the production of raw materials (e.g. carbon dioxide or the aluminium oxide used) and also to a large extent in the final management of waste streams. However, these impacts get almost compensated by the emissions avoided in the production of the alumina by-product.

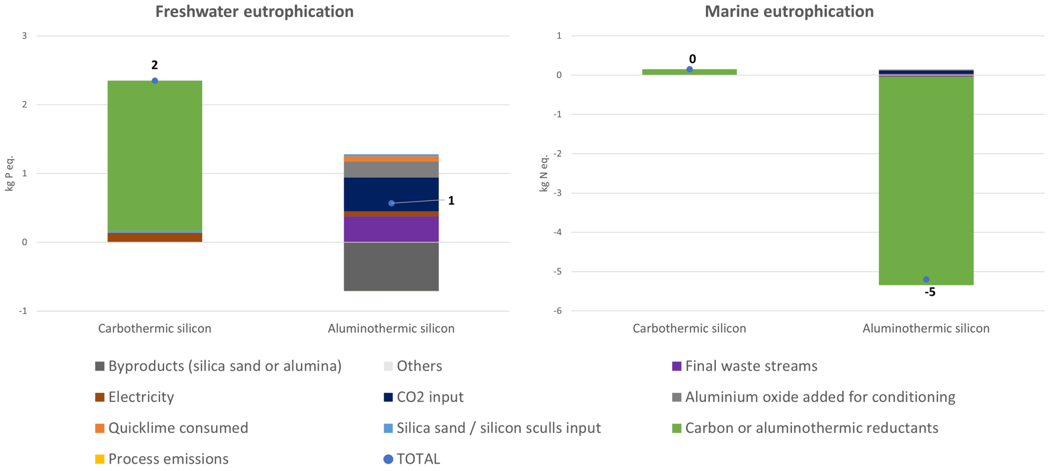

Figure 4.4: Comparison of the freshwater and marine eutrophication impacts for the aluminothermic and carbothermic processes. Expressed in kg P and kg N equivalent, respectively. F.U.: 1 tonne of silicon after ladle refining in Norway.

Regarding **marine eutrophication impact** (in Figure 4.4 - right graph) none of the silicon production routes account for a significant positive impact to this impact category (note that the numbers in the graph display rounded values and the carbothermic silicon route accounts for approx. 0,15 kg N equivalent). The aluminothermic route, however, displays a negative contribution to this environmental impact category. The reason behind this negative contribution is found in the impact avoided by the use of the aluminium drosses as input materials. Removing aluminium drosses from the end-of-life waste streams avoids the release of nitrates and other eutrophication drivers which are contained in the drosses and released through leaching in the landfills.

4.1.4 Terrestrial acidification and ecotoxicity

Terrestrial acidification impact (Figure 4.5 – left graph) is strongly influenced by the emissions of the furnace in the conventional silicon production route, accounting for more than 80% of the impact attributed to this route. This impact is largely caused by the emissions of SO_2 (and other acidifying emissions) released through the fumes. The input of hard coal represents the major part of the remaining impact associated with this impact category, which is found strongly influenced by the emissions of these pollutants in the transportation of coal from international maritime shipping.

The impact in the aluminothermic system is lower and more evenly distributed between the different unit processes. It is mainly caused by the impact of the emissions during the production of aluminium oxide, quicklime, carbon dioxide or pig iron (for underground container) inputs. However, the emissions avoided in the production of the alumina by-product can discount a large impact from this impact category.

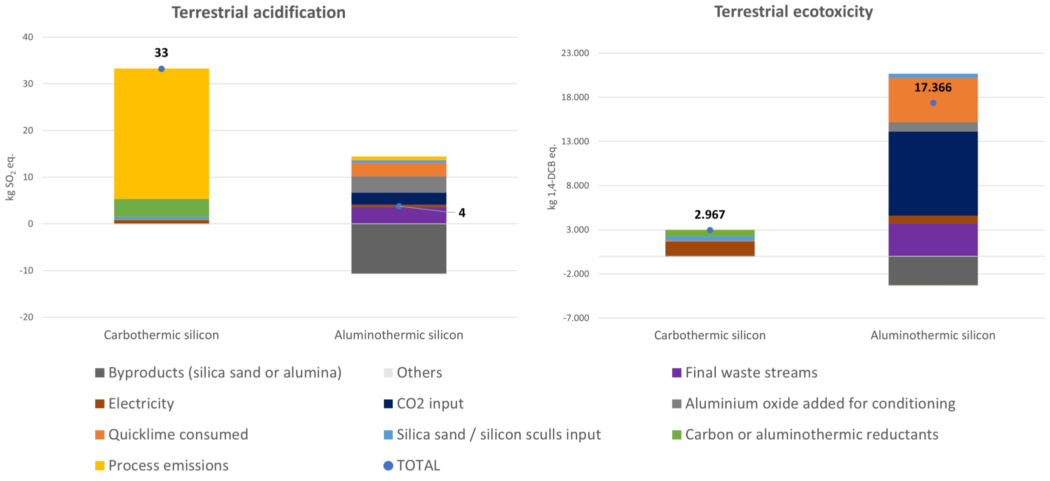

Figure 4.5: Comparison of the terrestrial acidification and terrestrial ecotoxicity impacts for the aluminothermic and carbothermic processes. Expressed in kg $SO_{2\ eq.}$ and kg 1,4-$DCB_{eq.}$, respectively. F.U.: 1 tonne of silicon after ladle refining in Norway.

In contrast to all the previously studied impacts, **terrestrial ecotoxicity impact** (in Figure 4.5 – right graph) scores higher for the aluminothermic silicon route. This is mainly attributed to the input of carbon dioxide (approx. 47% of the impact), quicklime (25%) and the hazardous waste management (18%).

The production of carbon dioxide owes its high impact to the emissions of monoethanolamine (these account for more than half of the impact associated with carbon dioxide). Monoethanolamine is used to absorb CO_2 in its production process but is then emitted to air, posing a high contribution to the ecotoxicity of terrestrial ecosystems.

The production of quicklime also releases emissions that contribute to terrestrial ecotoxicity, as it involves emitting air pollutants that are well-known precursors of the terrestrial ecotoxicity impact, like vanadium, nickel or copper.

Lastly, the hazardous waste management process also involves the emissions of these pollutants mainly in the transportation from lorries and in the construction of the steel underground deposit.

The emissions avoided by the alumina by-product are substantial but do not compensate for the aforementioned impacts.

Regarding the carbothermic route, the impact is mainly associated with the production of the electricity consumed, but the overall emissions are significantly lower than in the alternative production route.

4.1.5 Freshwater and marine ecotoxicity

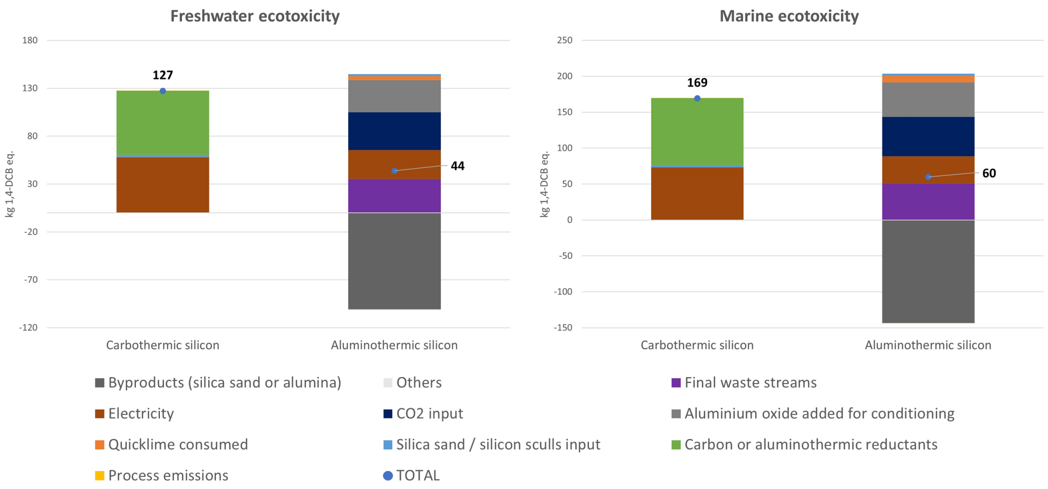

Figure 4.6: Comparison of the freshwater and marine ecotoxicity impact for the aluminothermic and carbothermic processes. Expressed in kg 1,4-$DCB_{eq.}$. F.U.: 1 tonne of silicon after ladle refining in Norway.

Freshwater and marine ecotoxicity (Figure 4.6) appear to be related to a large extent with emissions from the carbon reductants and the electricity consumed in the carbothermic route. The first is mainly attributed to the treatment of the spoil from hard coal mining, as emissions to water occur from the leaching in landfills. Electricity consumption, on the other hand, affects these impact categories mainly in the treatment of the residues from the construction of the transmission networks.

The aluminothermic silicon production performs better in this environmental impact category as its impact score is slightly over the carbothermic route (counting with all impacts from electricity, final waste streams, carbon dioxide input or aluminium oxide consumed) but it also gets partially compensated by the emissions avoided in the production of the alumina by-product.

4.1.6 Human carcinogenic and non-carcinogenic toxicity

Human carcinogenic toxicity (in Figure 4.7 - left graph) poses a higher risk to the carbothermic silicon production route. This is strongly linked to the carbon reductants used in the carbothermic route (more than 80% of the impact) associated especially with the use of hard coal and the emissions from leaching of the spoil from mining in landfills.

In the aluminothermic route, almost 65% of the human carcinogenic toxicity impact is caused by the consumption of aluminium oxide. However, the production of alumina as a by-product can reduce the overall impact by two times the positive impacts, therefore resulting in a net negative impact when considering the avoided emissions of by-products. The carcinogenic toxicity avoided by the production of alumina is related to the digestion of red mud in landfills, which would involve the emission of carcinogenic compounds.

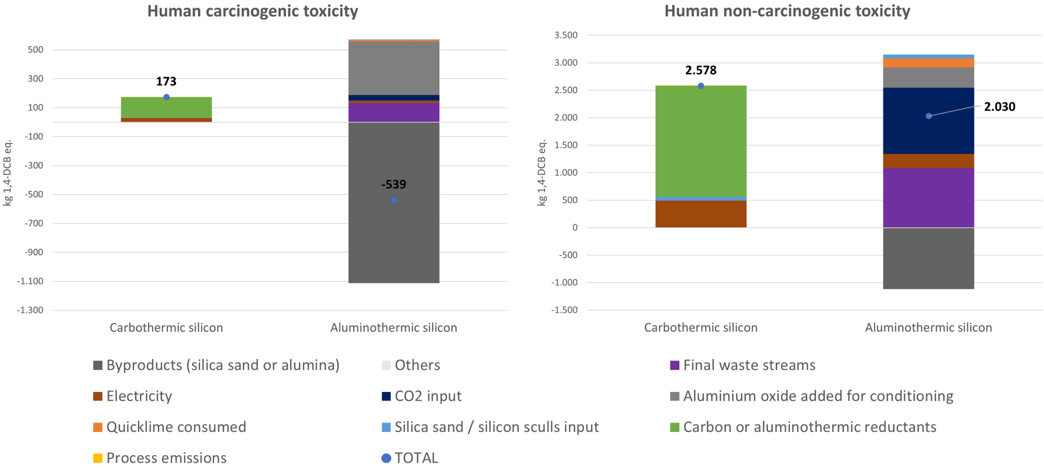

Figure 4.7: Comparison of the human carcinogenic and non-carcinogenic toxicity impacts for the aluminothermic and carbothermic processes. Expressed in kg 1,4-$\text{DCB}_{\text{eq.}}$. F.U.: 1 tonne of silicon after ladle refining in Norway.

Human non-carcinogenic toxicity (in Figure 4.7 - right graph) is attributed to the use of carbon reductants in the carbothermic route (especially to the use of hard coal, accounting for almost 80% of the total contribution). This is associated with the leaching from the spoil in hard coal mining. The majority of the remaining impact in the carbothermic route is associated with the electricity consumed and related to the municipal waste incinerators.

The impact in the aluminothermic route is lower when accounting for the emissions avoided by the production of alumina. The impact to this category is overall associated with the input of carbon dioxide (accounts for non-carcinogenic emissions in the construction of the plant, due to the high use of copper) and also to the treatment of the final waste streams.

4.1.7 Mineral and fossil resource scarcity and land-use

Mineral resource scarcity (Figure 4.8 - top left graph in the next page) is not highly impacted by the carbothermic production route, and however, this impact category still displays a lower contribution in the aluminothermic route, mostly because the alumina by-product avoids the extraction of raw bauxite.

Figure 4.8 (top right graph) displays the **fossil resource scarcity impact** following the carbothermic and aluminothermic production routes. The carbothermic route accounts for a high impact in this category, due to the use of carbothermic reductants (almost 90% of the impact). In the aluminothermic production route, the impact is closely associated with the quicklime, aluminium oxide and carbon dioxide consumed, as well as the management of final waste streams, as all these unit processes consume petroleum, natural gas or coke during their life cycle. However, the impact avoided by the production of alumina in this impact category can reduce the overall impact by more than a third.

Land-use impact (Figure 4.8 - bottom graph) is greatly affected by the carbothermic route and in more than 80% attributed to the selection of woodchips as carbothermic reductants. In the aluminothermic route, the impact is lower and mostly associated with hazardous waste management (in more than 75%) and this is due to the use of sawn wood in the underground deposit. This impact category seems to be closely related to the wood input to the process and therefore is considered more uncertain since the selection of a different carbon reductant would greatly affect the results of the assessment.

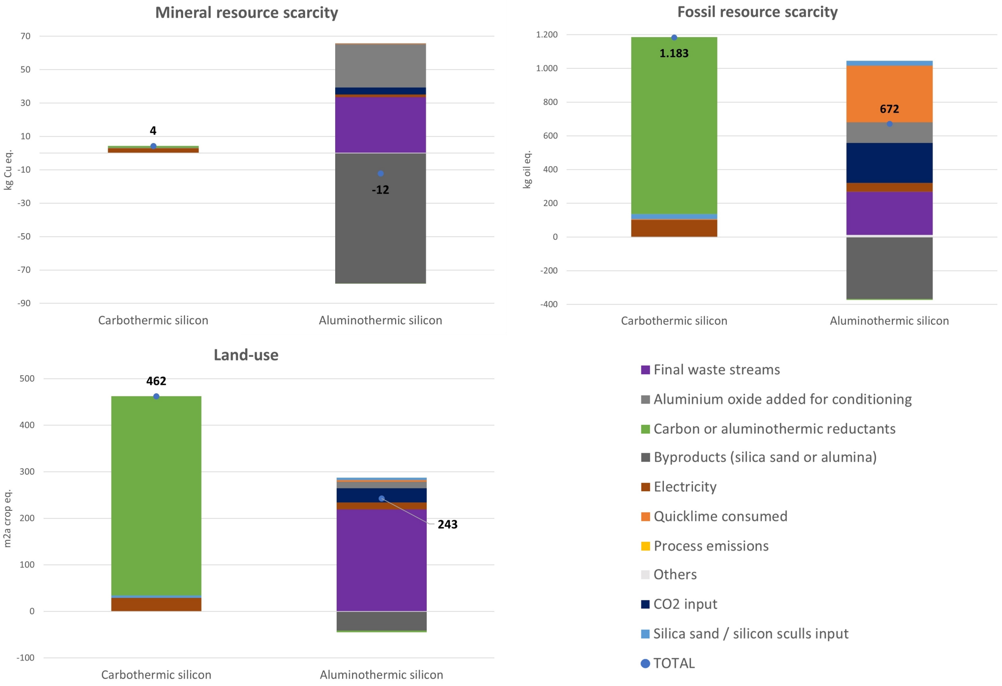

Figure 4.8: Comparison of the mineral and fossil resource scarcity and land-use impacts for the aluminothermic and carbothermic processes. Expressed in kg $Cu_{eq.}$, kg $oil_{eq.}$ and m2a $crop_{eq.}$, in this order. F.U.: 1 tonne of silicon after ladle refining in Norway.

In Appendix D the impact results are displayed both as characterization results and normalised results (Tables D.1 and D.2). Normalization is not a mandatory step in a Life Cycle Assessment but allows the comparison between impact categories as it expresses the LCIA results relative to those of a reference system [58]. ReCiPe uses a World normalization reference, by comparing the results with averages of per capita emissions. Normalised results are discussed later as they are used as a basis for the sensitivity analysis (in Chapter 4.3).

4.2 Contribution to endpoint categories

Endpoint impact categories have the advantage of expressing more condensed information related to the different Areas of Protection, allowing for an easier decision-making process. Midpoint results are usually more difficult to interpret, due to the large number of impact categories considered, however they are also more useful to identify trade-offs and impacts with more detail, as it has been done throughout Section 4.1. The combination of endpoint and midpoint categories in this study will allow the balancing of both types of results to reach an informed conclusion.

The indicators assessed at an Endpoint level in the ReCiPe methodology are three: human health, ecosystems, and resources availability. To be able to compare endpoints, after results are normalized, these are weighted. Average weighting factors used for the hierarchist perspective (H/A) in the ReCiPe method value equally human health and ecosystems, but the relative importance of the resources category holds half this value. The default weighting set is as follows:

- Human health 40%.
- Ecosystems 40%.
- Resources 20%.

The results of this assessment expressed in terms of weighted endpoint categories (Pt) are pictured in Figure 4.9.

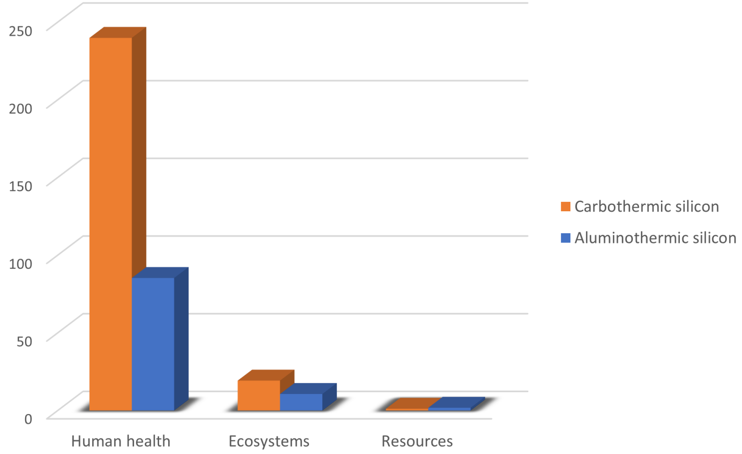

Figure 4.9: Comparison of endpoint impacts. Expressed in weighted points. F.U.: 1 tonne of silicon after ladle refining in Norway.

In Figure 4.9 it can be appreciated that both human health and ecosystems impact categories are affected to a much larger extent by the carbothermic route. This result is in accordance with the results displayed by the midpoint impact categories' analyses, as all impact categories except for terrestrial ecotoxicity accounted for a smaller impact in the aluminothermic route.

However, it can also be observed that the resources impact category is slightly more affected by the aluminothermic silicon production route (1,76 Pt vs. 1,12 Pt in the carbothermic route). This would contradict the categories related to damage to resource availability at the midpoint level (that is, mineral and fossil resources) as both impact categories displayed a lower contribution for the aluminothermic system, and midpoint to endpoint conversion factors are constant per impact category (the environmental mechanisms that affect endpoints are considered identical for all the stressors [76]). An explanation for this result is found when analysing closely the inventory considered by the ReCiPe (2016) Midpoint and Endpoint methodologies. While ReCiPe Midpoint studies 21 substances affecting fossil resource scarcity, ReCiPe Endpoint involves only the assessment of 19 different substances. The substances that are excluded from the analysis of endpoints include brown coal and peat. As the carbothermic route relies more heavily on fossil resources, this category decreases also to a higher extent when these resources are not included in the assessment. The reason why brown coal and peat are not included in the assessment of the endpoint could be due to a lack of mid-to endpoint characterization factors for these substances.

Despite this difference, when considering all endpoint impact categories together the aluminothermic silicon production route still contributes less to the overall endpoint impacts, as can be observed in figure 4.10.

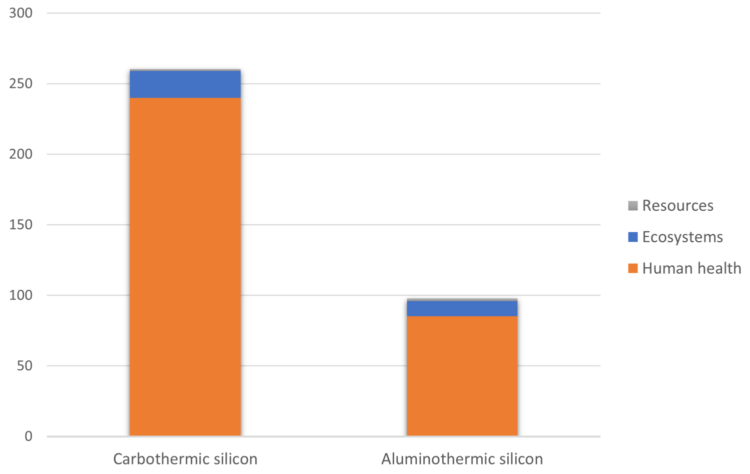

Figure 4.10: Comparison of endpoint impacts (aggregated figure). Expressed in weighted points. F.U.: 1 tonne of silicon after ladle refining in Norway.

The impact results for the endpoint assessment as well as normalized and weighted results are displayed in Table D.3 in Appendix D.

4.3 Uncertainty and sensitivity assessments

The results of this assessment need to be both analytically and numerically evaluated, as to be interpreted considering the limitations of data and the scope of the study:

- **Limitations regarding data availability.** An LCA assessment on the implementation of the SisAl Pilot holds a great uncertainty regarding data availability, as the experimental evaluation of this process is still ongoing. This study, however, is conducted based on process simulation models and data on the companies' raw materials, which are valuable to develop the inventory according to stoichiometric simulations but could face difficulties when implementing the process on a large scale (e.g. due to energy losses during the process in real conditions). Even though numeric models have been comprehensively implemented to try and evaluate all possible material and energy losses during the process, these will not be known with certainty until the experimental evaluation takes place. The fact that LCA is an iterative process will allow for implementing the necessary corrections to the inventory when this is improved.

- **Limitations of model assumptions.** The model assumptions might also be modified in future studies of the aluminothermic reduction process, e.g for this study, the system boundaries include refining of both carbothermic and aluminothermic silicon in a ladle. In reality, it is still not known if the aluminothermic process should still face further refining (if the product of the aluminothermic production after ladle refining would not have reached the necessary quality). This might modify the results of the assessment to a certain extent, and should be evaluated when the information is available. Besides, for certain inputs and outputs, an overestimation of the impact may have taken place. When the input and output materials were not available in ecoinvent, the worst-case scenario has been chosen (e.g. when considering a waste flow hazardous, or when using silica sand instead of silicon skulls). This was done to not underestimate the carbothermic route when compared to the aluminothermic one. In this way, the results are more valuable to reach a conclusion. However, when the composition and toxicity of the materials are better studied, these flows should be modified to account for more precise results.
- **Limitations regarding data accuracy.** The data included for this assessment involves an inherent uncertainty regarding the time, spatial and technological perspectives. For instance, the LCIA ecoinvent 3.5 database considers characterization factors that have not been updated since 2018. Similarly, some of the emission factors that were used correspond to certain locations, years, or technological levels that may not correspond with the reality of this assessment. However, the author has used to the extent possible the data that better represented the conditions defined by the Goal and Scope, which were also available. The emission and characterization factors should be updated in future studies to reach better results.
- **Limitations regarding the scope of the study.** This LCA is considering certain conditions that if modified would affect the assessment. This is the case, for instance, regarding the geographical scope or the raw materials. These are analysed in the sensitivity analysis to test the sensitivity of the results to different conditions.

Over this Chapter, the uncertainty and sensitivity assessment of this LCA are further analysed in Sections 4.3.1, 4.3.2 and 4.3.3.

4.3.1 Uncertainty of results

As it has been discussed, the limitations of this research regarding data availability, model assumptions, data accuracy and scope of the study increase the uncertainty of results, and the iterative nature of LCA assessments should allow for further refinement of the comparison of carbothermic and aluminothermic silicon production routes in the future.

While more experimental and process modelling is taking place, it is still important to compare the uncertainty in the carbothermic and aluminothermic systems. In terms of process emissions, it needs to be considered that there is much more information available regarding the carbothermic (conventional) silicon production route, and this production route is, therefore, less uncertain, as even though emissions of carbon dioxide and water vapour are calculated based on process modelling in HSC, the background data that this programme considers is likely to be more accurate for the carbothermic production route. In addition, other emissions considered for the assessment (e.g. methane, NOx) are based on scientific literature for the carbothermic route while the aluminothermic emissions are derived from internal estimations in the SisAl Consortium and therefore are also more likely to change when experimental modelling is further implemented.

Another major source of uncertainty in this comparison concerns the quality of the silicon product. Over this study, it has been mentioned that the composition of the silicon produced by aluminothermic reduction has not been closely studied yet. The process modelling indicates that using aluminium dross as a raw material may pose a problem since it contains elements that are not completely removed by ladle refining (e.g. Fe, P, Mn), and therefore the obtention of the purest forms of silicon would require the input of other raw materials. To be able to compare the carbothermic and aluminothermic routes, it has been assumed that the product of both routes displays similar qualities during this assessment.

Taking into account the above considerations, the aluminothermic system impact is, therefore, subject to change more than the carbothermic route when future LCA assessment takes place. The assumptions developed throughout this study have intended to consider the worst-case scenario for the aluminothermic route, whenever a value was not known in a range of values (namely, when considering that a waste flow from the aluminothermic reduction was hazardous or when silica sand was used as an input to the process instead of silicon skulls). These unit flows account for a bigger environmental impact than the alternative but this overestimation is intended to show the worst possible result for the aluminothermic reduction, as then if the result is better than in the carbothermic route it would still be more valuable for the conclusions. This would also indicate that the aluminothermic results could be overestimated rather than underestimated. Despite this fact, it is also known that process models usually consider ideal conditions that are not replicated on large-scale production systems, and do not account for other practical conditions that may take place when the operations are carried out (e.g. if the separation between the metal and slag phases is easily performed could depend on its viscosity). Therefore, it is yet to be studied the influence of these conditions and experimental assessment to validate the theoretical results. However, the main conclusions of this LCA are considered to not vary greatly as the uncertainty of this assessment is linked to practical conditions rather than to the amount of emissions or material consumption.

4.3.2 Sensitivity to the electricity mix

In this LCA, the Norwegian electricity mix was used to account for the production conditions in Norway. It has been studied that electricity consumption holds a great impact for some impact categories. As the SisAl Pilot is expected to be implemented in other countries as well, the results are tested with the application of the European electricity mix to test how sensitive is the system to the electricity mix and if that could change the preferred option.

The results of this substitution are displayed below in Figure 4.11.

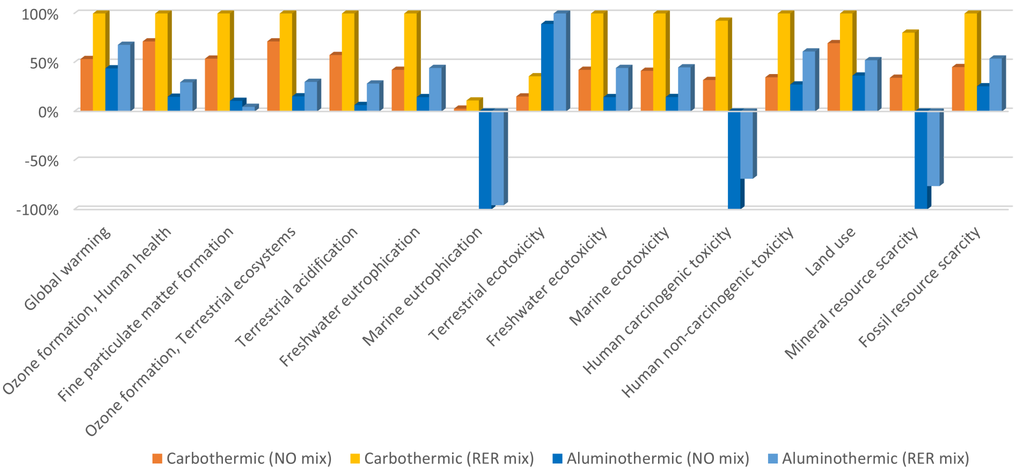

Figure 4.11: Impact results using the Norwegian and European electricity mixes.

The overall trend shows that the European electricity mix (RER mix) influences to a great extent the results, causing a higher impact for both the carbothermic and aluminothermic routes than when using the Norwegian electricity mix. This is explained because the Norwegian electricity mix relies heavily on hydropower [83], which display relatively low characterization factors for all impact categories.

Despite this fact, the application of one or the other electricity mix does not change the preferential silicon production route for any impact category, meaning that the

SisAl process would generally be valuable even when using other electricity mixes. Looking into the contribution per process in the baseline scenario (Table D.4 in Appendix D) it is outstanding that the aluminothermic route is less dependent on the electricity mix (12,33% of the impact compared to 37,45% of the impact in the carbothermic route). The aluminothermic reduction is exothermic and therefore it also needs less energy input to the process. Thus, as a general rule, the carbothermic route also gets more affected by an increase in the electricity specific characterization factors.

Detailed results of the sensitivity analysis regarding electricity consumption are displayed in Table E.1 in Appendix E.

4.3.3 Sensitivity to the reductant material

When analysing the normalised results (in Table D.4) it is noteworthy that the reductants used also hold a great impact on the impact assessment. In the carbothermic route, a mix of hard coal and woodchips is used. Hard coal has been identified throughout the contribution analysis as one of the largest contributors to most impact categories. On the other hand, woodchips appear only relevant to the land-use category (less than 3% of the impact for the rest of the impact categories). In addition, woodchips are also considered to release biogenic CO_2 emissions, which do not contribute to the GWP as these emissions were previously captured from the air in the growing of biomass. The mix of reductants considered in this study is a typical composition used by the industry that is assumed to not vary greatly between different producing companies or locations.

On the other hand, the emissions avoided by the use of aluminium dross as a reductant in the aluminothermic production route will be modified if other aluminium reductants are consumed. As this raw material can be easily substituted by the producing companies, it is interesting to study the effects that the application of post-consumer aluminium scrap would have on the overall impact.

To model this, the input of aluminium dross is substituted by an input of post-consumer aluminium scrap, i.e. "Aluminium, cast alloy (RER) | treatment of aluminium scrap, post-consumer, prepared for recycling, at refiner | APOS, U" as in ecoinvent. Note that only this flow is substituted in the simulation and the rest of the emissions that silicon production involve are not modified. The results obtained are therefore not accurate but allow for a rough comparison on the application of various aluminium sources while the detailed inventory is still not available.

The results of this assessment are introduced in Figure 4.12 on the next page.

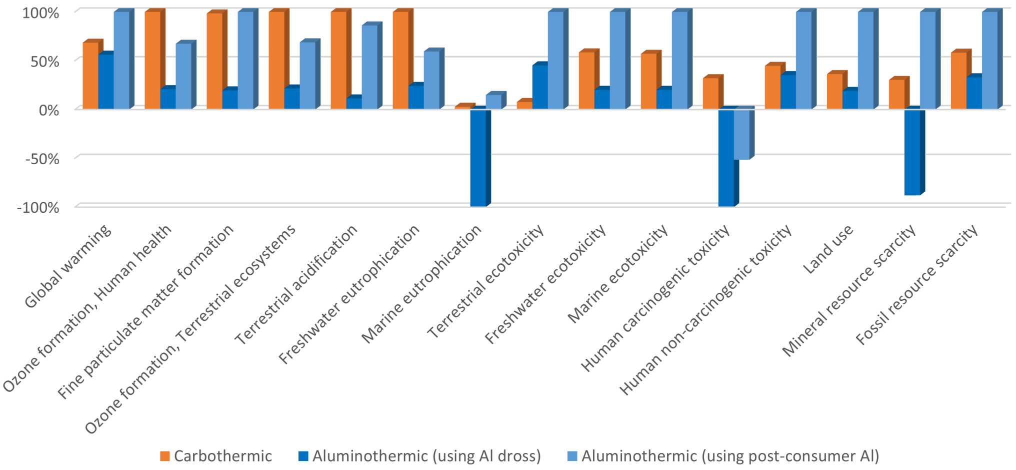

Figure 4.12: Impact results using post-consumer aluminium scrap as an input.

The assessment results when using post-consumer aluminium scrap show an increase of the impact in all impact categories when compared to the aluminothermic route using Al dross as an input. Even when compared to the carbothermic reduction, there is still an increase for many of the impacts, namely global warming, fine particulate matter formation, land use, mineral and fossil resource scarcity and human non-carcinogenic, terrestrial, freshwater and marine toxicities.

It is analysed that the input of aluminium scrap holds a bigger contribution for many impact categories since it is considering that these aluminium residues, when diverted from the recycling stream, would affect the availability of aluminium for recycling, obtaining a decrease in this material and therefore more primary aluminium would need to be obtained from primary raw materials. Unless there is an overflow of aluminium from downgraded materials such as end-of-life vehicles, as some scenarios predict in the future [38], post-consumer aluminium scrap would better be used in the production of recycled aluminium, based on the results of the impact assessment.

In this regard, it is also important to mention that ecoinvent applies a global scope, and from a European perspective aluminium post-consumer scrap is already being exported to other parts of the world, with the associated costs. As it is not being used for recycling in Europe, the environmental impact attributed would be much lower within this geographical scope. Future modelling of the SisAl process should explore how to include the reality of the European market in the environmental assessment of silicon production in Europe.

Detailed results of the sensitivity analysis when using post-consumer scrap as an input can be found in Table E.2 in Appendix E.

4.4 Future influence of the SisAl process

4.4.1 Possible improvements to the aluminothermic system

Other modifications to the SisAl Pilot to decrease even further the impact of this silicon production route include:

1. Calcium carbonate is produced in the hydrometallurgical route as it is the major component of the residual precipitate from the $CaO \cdot SiO_2$ separation. This flow could be further processed into limestone and recirculated back for its use in other parts of the system.
2. The SisAl refining slag could be recirculated as raw material for its use as silicon skulls since these flows also present similar composition (in terms of CaO and SiO_2 content).

Therefore, the two flows considered above, that were in the baseline scenario considered as inert waste, could be modelled as follows:

Table 4.1: Processes substituted by the recirculation of materials in SimaPro.

Input / Output	**Amount**	**Comment**
Calcium carbonate, precipitated (RER) | market for calcium carbonate, precipitated | APOS, U	1,32 t	This flow is further processed into limestone and recirculated back for its use in other parts of the system, but as this part of the system has not been modelled yet, for simplicity it is considered a by-product in the assessment. It substitutes a flow of inert waste.
Silica sand (GLO) | market for | APOS, U	1,59 t	The amount is calculated from the input of silica sand (2,58 tonnes) minus the SisAl refining slag (0,99 tonnes) because this is recirculated as raw material. Also substituting a flow of inert waste.

The results of this assessment can be appreciated in Figure 4.13 on the following page.

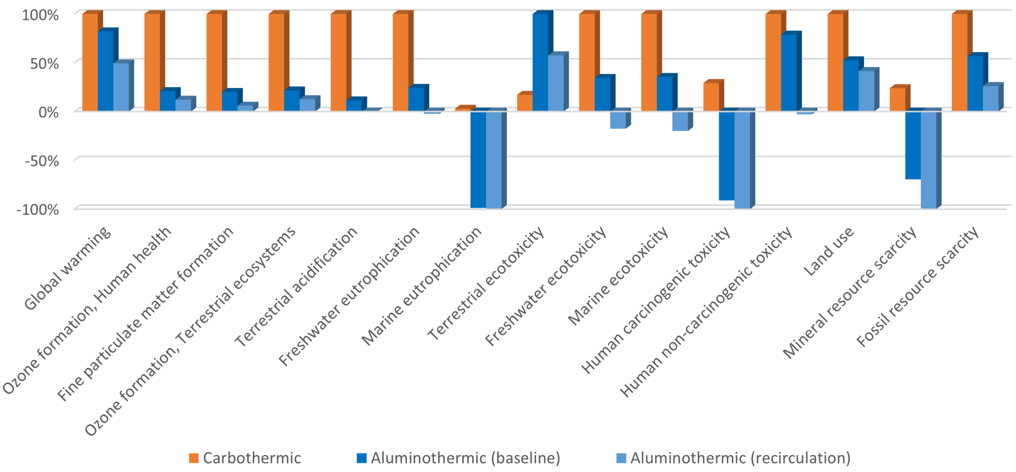

Figure 4.13: Impact results following the recirculation of materials.

By applying these modifications to the baseline aluminothermic silicon production route it can be observed that the overall impact is reduced for all impact categories, which indicates that the recirculation of these flows would be a potential advantage for the implementation of the SisAl Pilot. However, as these flows have not been experimentally evaluated yet, it has been decided that the recirculation of materials would not be evaluated as the main scenario, since it is more valuable to know that even if the materials are not recirculated the process is still valuable from an environmental perspective.

Detailed results can be found in Table E.3 in Appendix E.

4.4.2 Scenarios of future aluminium waste flows and Si production

Currently, the secondary materials generated in the production and waste streams for silicon and aluminium in Europe amount to 45.000 tonnes/yr of silicon skulls, 70.000 tonnes per year of Al dross, and 900.000 tonnes/yr of post-consumer aluminium scrap that is being exported (only in Europe - see Chapter 2 for references). As it has been studied, the production of 1 tonne of aluminothermic silicon requires 2,58 tonnes of silicon skulls and 0,87 tonnes of aluminothermic reductant (see inventory in Table 3.2). It can be calculated that the limiting factor regarding the secondary input of raw materials lays in the availability of Si skulls. However, as it has been mentioned throughout the research, silicon skulls still hold value for the producers of silicomanganese and it is found that the input of silicon from primary sources (i.e. silica sand) does not pose a big contribution to the results of the impact assessment (1,21% - in Table D.4). Therefore, it is considered for this assessment that the secondary source of Al is the limiting factor for the aluminothermic production of silicon. In this case, the selection of different sources of aluminium, as it has been studied during the sensitivity analysis in Section 4.3.3, holds a major influence on the results.

In 2020, silicon production worldwide ascended to 8 million tonnes [84]. The Norwegian production is estimated to amount 4% of this production (figure for both silicon and ferrosilicon combined [13]). Considering the quantity of aluminium post-consumer scrap available in Europe and the necessary input of aluminium to the SisAl process, this material could provide for the entire production of silicon in Norway. However, the use of aluminium dross as a reductant material has been studied to be more sustainable when assessing the overall impacts from a global perspective and therefore this will be the basis for the scenario analysis.

The use of aluminium dross alone would allow for much lower production of silicon (around 25% of the Norwegian production, considering an input of aluminium dross from the rest of Europe). Regarding the global warming impact, the net influence of the aluminothermic reduction using this input material is the avoidance of 1.119 kg CO_2 equivalent per ton of Si produced by aluminothermic reduction, meaning more than one tonne of CO_2 equivalent is avoided per tonne of Si produced following the aluminothermic route. That is a decrease of approximately 18% of the global warming impact compared to the carbothermic route.

As it has been argued throughout Chapter 2 estimating the future demand of silicon can result in a complex task due to its disperse use and many applications. For this reason, the approach taken by Eric Williams in “Forecasting material and economic flows in the global production chain for silicon” [52] is followed (Equation 4.1). This considers that the forecast for future silicon material flows can be estimated with a relatively high degree of confidence by looking at longer trends. The exponential growth model applies a growth of 3,5% yearly (g), being t the time difference in years.

$$Production(t) = Production(0) \times (1+g)^t \tag{4.1}$$

After the application of Equation 4.1, and considering as a baseline the global production in 2020, future global demand of Si metal obtained for 2030 results in 1,4 times the current figure. If the aluminothermic reduction system using Al dross is applied in Norway by 2030, assuming that Norway still produces 4% of the calculated demand and that the ratio Al dross produced per unit of aluminium is constant (and aluminium production grows at least proportionally to that of Si) then the emissions avoided by the application of the aluminothermic route for producing silicon would ascend to 127.047 tonnes CO_2 equivalent, only in 2030. If this figure is compared to the target of reducing GHG emissions by at least 40% by 2030 from 1990 levels [85, 86], then the application of the SisAl process would achieve almost 10% of this reduction for the ferrosilicon industry (in Norway) (reference for 1990 levels can be found in the National Inventory Report from the Norwegian Environment Agency [87]). A summary of these results is displayed in Table 4.2.

Table 4.2: Data for the scenario of aluminium waste flows and silicon production (applying baseline aluminothermic reduction process).

	2020	2030
Generation of Al dross (Europe)	45.000 t	98.741,91 t
Potential aluminothermic Si production	80.459,77 t	113.496,45 t
Percentage of total production in Norway	25,14%	25,14%
Emissions avoided (t $CO_{2\ \mathrm{eq.}}$)	90.066,16	127.047,21
Target fulfillment	–	9,8%

Considering the impact results from the model in which certain flows were recirculated inside the process, this contribution would amount even higher ascending to 27% of the required reduction (Table 4.3).

Table 4.3: Data for the scenario of aluminium waste flows and silicon production (results for the recirculation of flows modification from baseline scenario).

	2020	2030
Emissions avoided (t $CO_{2\ \mathrm{eq.}}$)	255.124,84	359.878,78
Target fulfillment	–	27,75%

These percentages prove to be a meaningful contribution to the required reduction of greenhouse gases in the silicon industry. It also needs to be considered that only aluminium dross is applied as raw material to this process and this is a limited resource, that otherwise would have low or even negative economic value, and more sources of aluminium should be explored for the SisAl process to be able to contribute even more strongly to sustainability, as well as the application of other strategies to complement the SisAl process (e.g. calcium looping with CCS, renewable energy technologies, or biocarbon use for the conventional production route).

4.4.3 Scenarios of biocarbon reductant feed

It has been studied in Chapter 2 that silicon producing companies are already working towards achieving carbon-neutral production, as e.g. Elkem has a 40% target of biocarbon use by 2030 [56]. Biocarbon, also known as charcoal, results from the thermal conversion of biomass, and therefore the use of this reductant would be considered to release biogenic emissions. This is the same reasoning that was applied previously to other organic materials that act as reductants in the carbothermic route (namely woodchips).

The move towards biocarbon materials as reductants in the carbothermic production would therefore avoid the release of carbon dioxide emissions into the atmosphere, in terms of LCA accounting. To model this transition, the hard coal content in the carbothermic reduction is gradually substituted by charcoal materials in Figure 4.14. Woodchips are maintained as in the baseline scenario since this source of reductant is already considered to release biogenic emissions. The unit process used to account for the use of charcoal in ecoinvent is: "Charcoal (GLO) | market for | APOS, U".

The methodology to estimate this release is the same as was used previously for woodchips (see Chapter 3.3). The use of charcoal is estimated to release 5,81 tonnes of biogenic CO_2 (if charcoal substitutes in 100% to hard coal). This process is repeated for the 80%, 60%, 40% and 20% scenarios. Detailed input and biogenic emissions calculated can be found in Table E.4 in Appendix E. In the simulations, total carbon dioxide emissions and the amount of reductant needed are maintained from the baseline scenario. This is intended to approximate the effect of biocarbon substitution in the reductants while the simulations to account for this reductant are not available yet, constituting a source of uncertainty.

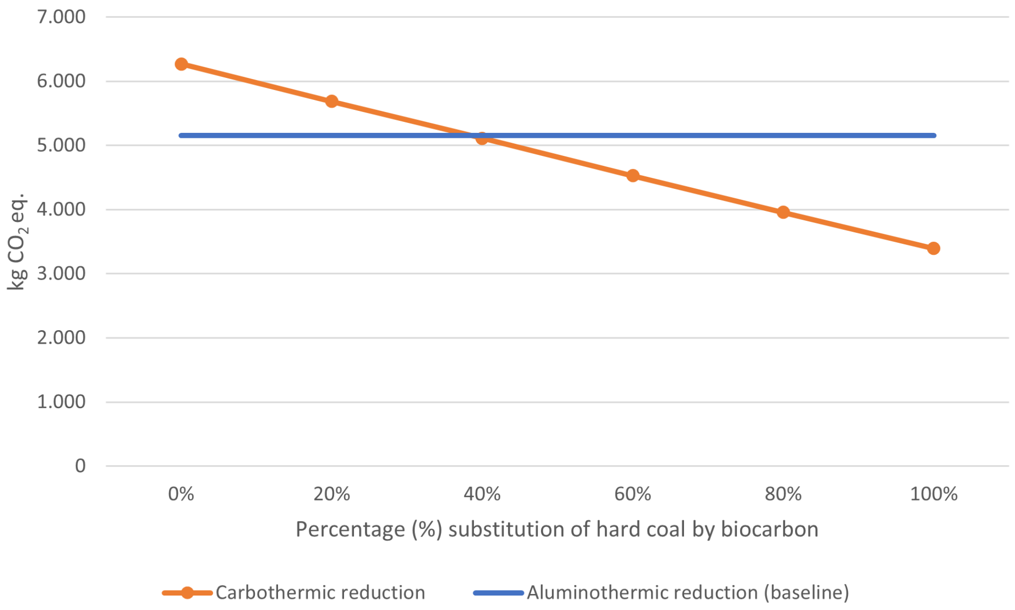

Figure 4.14: Biocarbon content influence in emissions.

In Figure 4.14 it is shown how the global warming impact decreases as hard coal in the carbothermic route is substituted by charcoal. Note that the emissions avoided in the 100% substitution scenario are lower than the number calculated above (5,81 tonnes). This is because hard coal is substituted by charcoal and this raw material accounts for a higher global warming impact in the production phase.

The point where the carbothermic and aluminothermic route have the same global warming impact is calculated to be in 38,68% substitution, and therefore a similar figure to Elkem's target. It should be pointed out that woodchips already accounted for 35% of the reductant feed in the furnace, and this is already a source of biogenic emissions. If woodchips were not used in the feed, this percentage would be substantially higher. Note that in the scenario in which flows are recirculated, the global warming impact of the carbothermic route using biocarbon does never get below the impact in the aluminothermic route for any percentage of substitution (below 3.098,18 kg $CO_{2\ eq.}$ - see Table E.3).

The main present barrier to the use of biocarbon in Norway is related to its high costs, as large amounts of charcoal are imported [88]. In addition, the only way in which the use of biocarbon can be sustainable when applied to the production of ferroalloys is if its production is also sustainable: deforestation and inefficient charcoal production could instead cause the undesired effect of a net increase in GHGs emissions [89].

In Figure 4.15 the overall impact categories studied are displayed for the scenario of completely substituting hard coal by biocarbon, and maintaining the composition of woodchips. It can be appreciated that even if the lowest impact of global warming is attributed to this substitution scenario, for other impact categories the variation is minimal (e.g. fine particulate matter or ozone formation). Land use impact is strongly affected by the use of biocarbon.

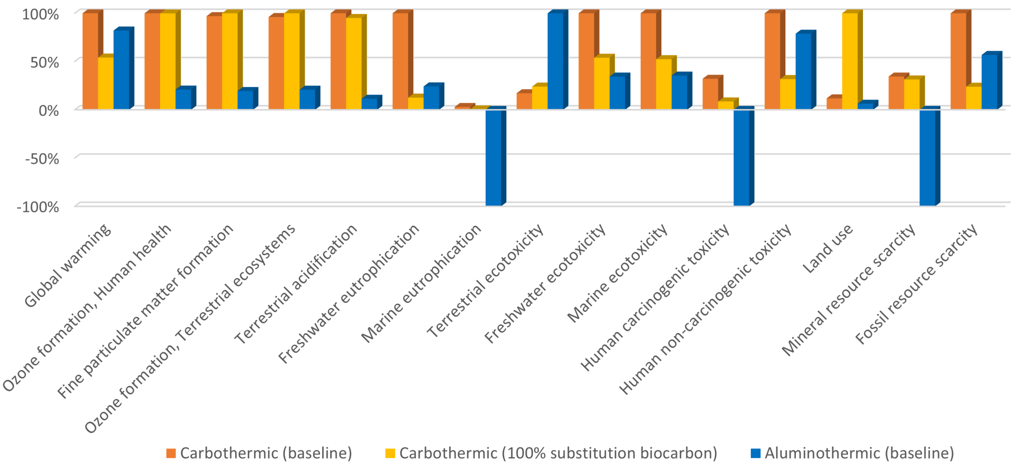

Figure 4.15: Impact results following a complete substitution of hard coal by biocarbon.

Detailed results for this assessment are found in Table E.5 in Appendix E.

Chapter 5

Conclusion

To better elaborate on the conclusions raised throughout this study, the research questions are discussed below:

What are the life cycle characteristics of the carbothermic and aluminothermic production of silicon (using silicon skulls and aluminium dross) in Norway, and the different contribution to the environmental impact between these alternatives?

Throughout this research, an LCA assessment has been developed to study the sustainability of both the carbothermic and aluminothermic silicon production routes. The data used for this assessment accounted for raw materials data (silicon skulls and aluminium dross) and process simulation models from companies in the SisAl Consortium. Results show a lower impact in the aluminothermic route for most of the studied impact categories, i.e. global warming, ozone formation, fine particulate matter formation, terrestrial acidification, freshwater and marine eutrophication, freshwater and marine ecotoxicity, human carcinogenic and non-carcinogenic toxicities, land use, and mineral and fossil resource scarcity. This decrease in the different impact categories is intricately linked to a reduced level of emissions from the furnace and energy consumption, as well as the emissions avoided by the production of alumina as a by-product and the consumption of aluminium dross as a raw material.

In the carbothermic route, the emissions released through the furnace, the carbon reductants used (especially the use of hard coal) and the electricity consumed are the hotspots for the different impact categories. In the aluminothermic route, the aluminium and carbon dioxide consumed in alumina refining and the final waste management account for most of the overall impact. Nevertheless, aluminothermic reduction appears to only be more damaging than the carbothermic route regarding the terrestrial ecotoxicity impact. This impact category is strongly influenced by the emissions of monoethanolamine, which are derived from the production of carbon dioxide. These emissions do not rely on the electricity mix, and therefore, it is not something that would be easily remediated with a future variation of the energy sources.

When assessing the endpoint categories, human health and ecosystems also display lower impacts in the aluminothermic route. Contrarily, it is studied that the impact on resources accounts for a bigger share than in the carbothermic route. This result, which would not agree with the respective midpoint categories fossil and mineral resource use, is obtained because the endpoint assessment excludes brown coal and peat from the analysis (which was previously included at the midpoint level). Therefore, the carbothermic route decreases its impact to a larger extent than the aluminothermic one. However, when studying the aggregated figure for all endpoints, the aluminothermic route still holds the lowest impact overall, accounting for less than half of the impact obtained from the carbothermic route.

Finally, a modification of the aluminothermic route that is intended to use the waste streams inside the process can reduce the impact of the aluminothermic route even further, by recirculating the inert waste as raw materials partially substituting the need for silicon skulls and limestone inputs. However, as these waste streams have not been experimentally characterised yet, this production route is not considered as the baseline scenario for the rest of the analyses developed.

How sensitive is the environmental impact of silicon production to the raw materials feed and changes in the electricity mix?

In a sensitivity analysis directed towards studying the influence of the electricity mix in the conventional and aluminothermic production of silicon, this is modified to reflect the European average. Results showed that when compared to the Norwegian mix, all impact categories present a higher contribution, being the carbothermic route more affected by these changes, as the aluminothermic production involves an exothermic reaction, and therefore less electricity needs to be provided into the system.

A key finding of this sensitivity analysis is that a change of the electricity mix to the European average does not modify the preferred alternative for any impact category, which would be relevant to scale up this technology to other locations.

A second sensitivity analysis tested the application of post-consumer aluminium scrap as an input for the aluminothermic route. This substitution produced a worse result for all impact categories scoring even higher than the carbothermic route for many impacts, which is explained because the input of post-consumer aluminium scrap holds the negative environmental effect of this scrap not being recycled and therefore an increased quantity of aluminium needs to be produced to answer this material demand. Contrarily to the use of aluminium dross, which application as raw material results beneficial for the environment, post-consumer aluminium as input material for silicon production presents a harmful contribution to all the studied impact categories.

Yet, the use of post-consumer aluminium scrap as input material for the SisAl project could be compelling considering 900.000 tonnes/yr of post-consumer aluminium scrap are currently being exported from Europe [27], and scenarios predict that this amount is likely to increase in the future due to an overflow of downgraded materials [38]. It is important to acknowledge that even if this assessment does not show promising results for the aluminothermic reduction using post-consumer aluminium scrap, ecoinvent also applies a global scope meaning that when looking only to Europe these residues are not being utilised and rather exported. Future regulations banning the export of aluminium post-consumer scrap could make the results look more benign for this raw material.

Lastly, the introduction of biocarbon as a reductant in the carbothermic process is tested to reproduce the future behaviour of silicon companies. The input of hard coal is substituted by charcoal during the scenario analysis, modelling different rates of substitution. The results of this assessment show that the "break-even point" in which the impact caused by GHG emissions are equal in the carbothermic and aluminothermic production routes using aluminium dross is found at a 38,68% substitution rate (considering the reductant material already involves 35% weight composition of woodchips). Most likely, to reach the target reduction set for 2030 a combination of both the substitution of hard coal as a reductant material and the production of silicon following the aluminothermic route would be necessary, as the aluminium reductant materials that can be used for the production of silicon are still limited.

How does the application of the SisAl Pilot further reduce the environmental impact of the silicon industry when considering future scenarios of aluminium waste flows and silicon demand?

Considering future scenarios of silicon demand and the current share of production from Norway, by 2030 the application of the aluminothermic route using aluminium dross could avoid the release of 127.047 tonnes of CO_2 equivalent. That accounts for approximately 10% of the target for greenhouse gas emissions in the ferrosilicon sector only in Norway by 2030.

If the scenario in which the waste streams of the aluminothermic reduction process are recirculated is evaluated instead, the contribution to the reduction of emissions would reach 27% of the required amount.

Over this study, it has been analysed that the aluminothermic reduction of silicon delivers promising results for its implementation in the production of silicon for Norwegian and European industries from an environmental perspective. In practice, the aluminothermic route may experience some problems e.g. regarding its large-scale implementation or the purity of the silicon obtained. For this reason, it is important to continue the experimental tests that are currently taking place in the different facilities and among the different partners of the SisAl Consortium. The obtention of experimental evaluation results will also allow reducing the uncertainty of the current LCA model on the aluminothermic reduction of silicon route using silicon skulls and Al dross, which has been evaluated, for the first time, in this master thesis.

On the other hand, using post-consumer aluminium scrap does not deliver many environmental benefits compared to the carbothermic reduction when applying a global scope, but it may be a better alternative within European boundaries if these waste materials are exported at low values, and especially if an overflow of post-consumer aluminium scrap is generated in future years.

With the production of silicon and aluminium being dominated by Chinese producers, there is a risk of carbon leakage if stricter environmental policies would increase the costs of production in Europe (e.g. with regards to carbon taxes or the EU-ETS scheme), thereby raising total emissions as production is moved to third countries with laxer standards. The use of secondary materials within Europe could maintain domestic production as the raw materials needed currently hold low economic value, potentially decreasing also GHGs emissions and associated costs.

To sustainably manage an increasing population requires the adoption of technologies that can minimize our impact on the planet. Silicon and aluminium have proven essential for this, with an important contribution as the main resources for the energy transition and digital economies. The opportunity for these industries lays in shifting towards industrial symbiosis, by utilizing the wastes from their production routes, and producing high-value products.

Despite the results of this master's thesis for the LCA assessment are susceptible to change with more experimental data, the conclusions are considered valid as the uncertainty of this LCA is overall related to the practical conditions of the process, rather than with the sources of emissions or materials input. Future research could look at expanding the model developed in this master thesis to include other raw materials as, for instance, SPL, or Si fines, especially since the availability of aluminium dross and Si skulls is limited.

Moreover, the integration of Material Flow Analysis (MFA) looking to the different aluminium and silicon secondary materials available with a spatial LCA would make it possible to measure the potential for implementation of the SisAl Pilot on a local scale, identifying regional impacts, opportunities and synergies with other sustainability aspects as the economic and social perspectives. This model extension would allow to better evaluate the use of post-consumer aluminium scrap and other reductant materials which application locally may be beneficial but that bear a high impact when applying a global perspective.

Throughout this master thesis, the benchmarking LCA of the aluminothermic reduction of silicon has been developed, and in particular, the effect of resourcing former waste streams from the silicon and aluminium industries has been evaluated. It is concluded that the implementation of the SisAl Pilot could potentially bring many environmental benefits to these industries, by reducing primary raw materials consumption, better managing the residues generated and producing highly valued products. However, this assessment has also pointed out that it is essential to study the sustainability of different raw materials for the aluminothermic production, as well as identifying their hotspots of pollution, before implementing this production system on a large scale, a step towards circular economy that minimizes the strain on the environment while maintaining the secure supply of materials that have proven essential for present and future generations.

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Appendix A

Life cycle for silicon and aluminium

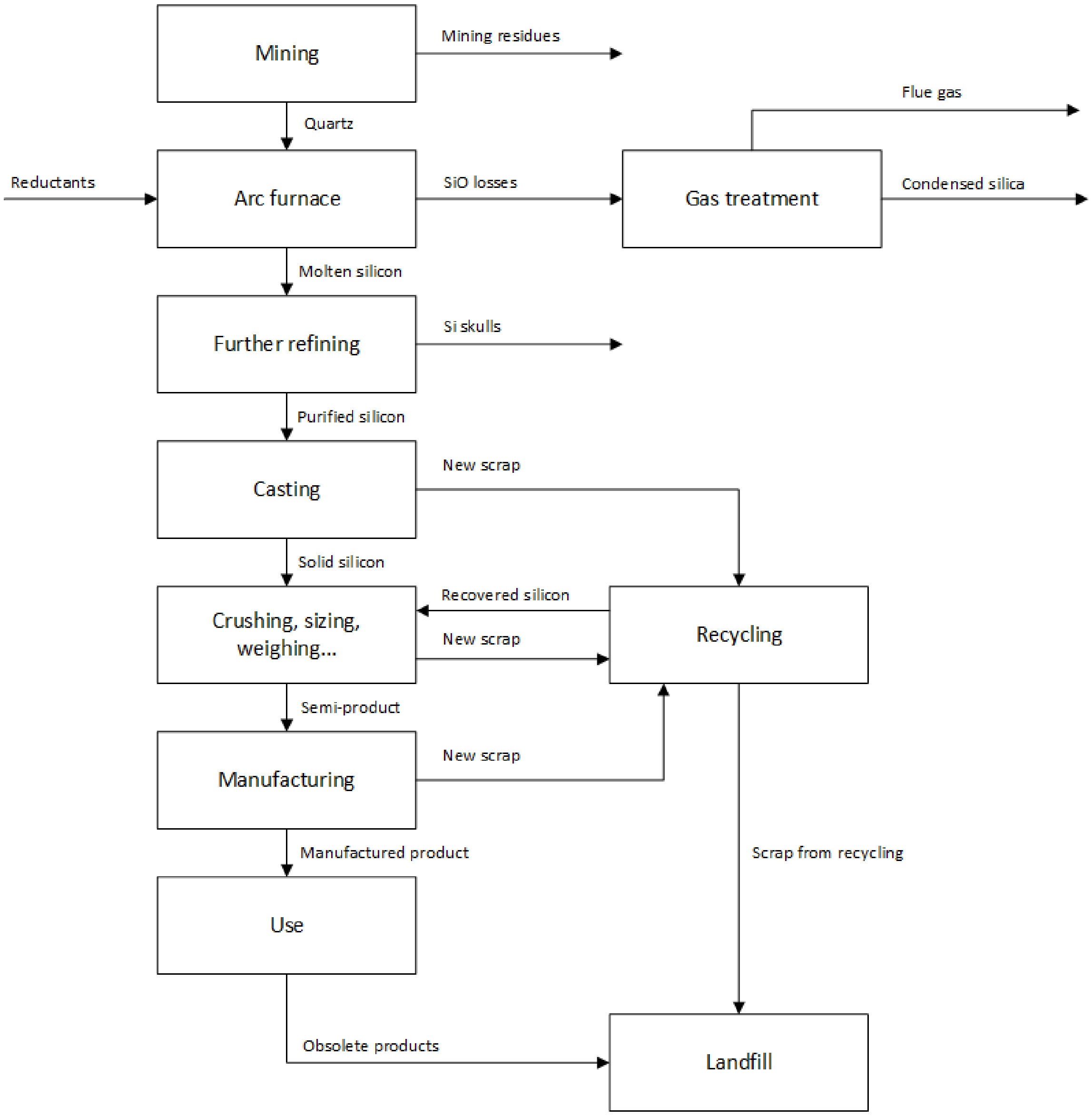

Figure A.1: Simplified life cycle for silicon metal, looking to the flow of Si.

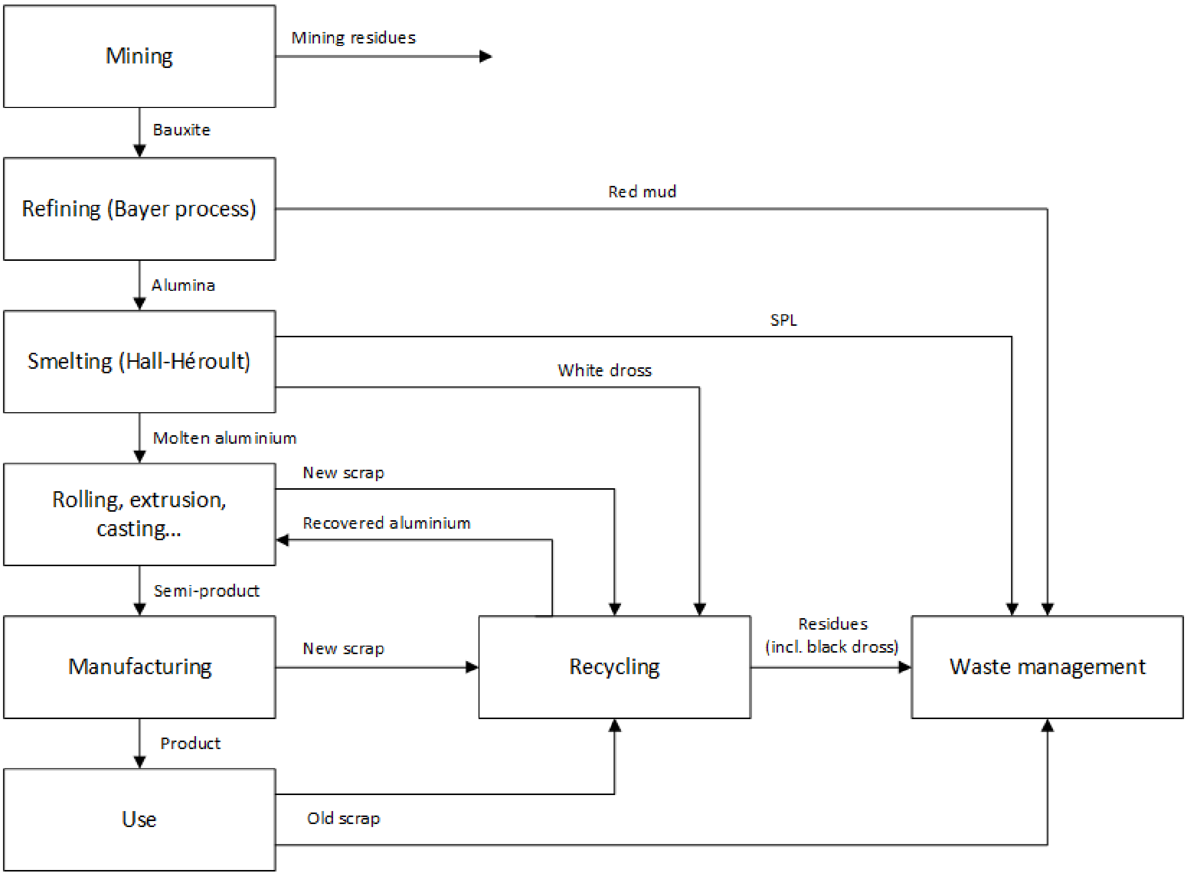

Figure A.2: Simplified life cycle for aluminium metal, looking to the flow of Al.

Appendix B

Literature data used in the LCI

Table B.1: Emission factors used to account for other pollutants in the silicon production.

Emission factors in Si production			
Substance	Data	Source	Comments
NOx	22 kg/t	[21]	Assumed to be a batch furnace type
CH_4	1,2 kg/t	[90]	Assumed to be the same than in ferroalloys production
Dioxins	3 μg/t	[91]	Assumed to be the same than in ferroalloys production
PAH	3 g/t		
$PM_{2,5}$	600 g/t	[92]	Assumed to be the same than in ferroalloys production
PM_{10}	850 g/t		

Table B.2: Content of trace elements in the raw materials. Adapted from “Material Balances of Trace Elements in the Ferrosilicon and Silicon Processes" [78] and "Chemical Composition of Wood Chips and Wood Pellets" [79]. When only the detection limit is given (e.g. <5 in some cases), it is estimated that half of this amount will enter the process, as no other value is known. Median values were preferred to mean values, to avoid the misrepresentation of outliers.

Raw materials content in trace elements				
Element	Hg (ppm)	S (ppm)	As (ppm)	Se (ppm)
Quartz	<5	927	0,3	<0,5
Woodchips	7,9E-04	75,5	0,05	4,3E-02
Coal	18	6.557	0,6	<0,5

Table B.3: Distribution of the trace elements between metal, silica and off-gas. Adapted from “Material Balances of Trace Elements in the Ferrosilicon and Silicon Processes" [78].

Distribution of the trace elements in the carbothermic reduction			
Element	% to metal	% to silica	% to filtered off-gas
Hg	0	60	40
S	15	10	75
As	30	65	5
Se	0	60	40

Table B.4: Carbon content of reductants for biogenic emissions. Information obtained from the ECN Phyllis classification database [93].

Reductant	Total carbon
Woodchips	49,60%
Charcoal	82,15%

Appendix C

Processes flowcharts in HSC

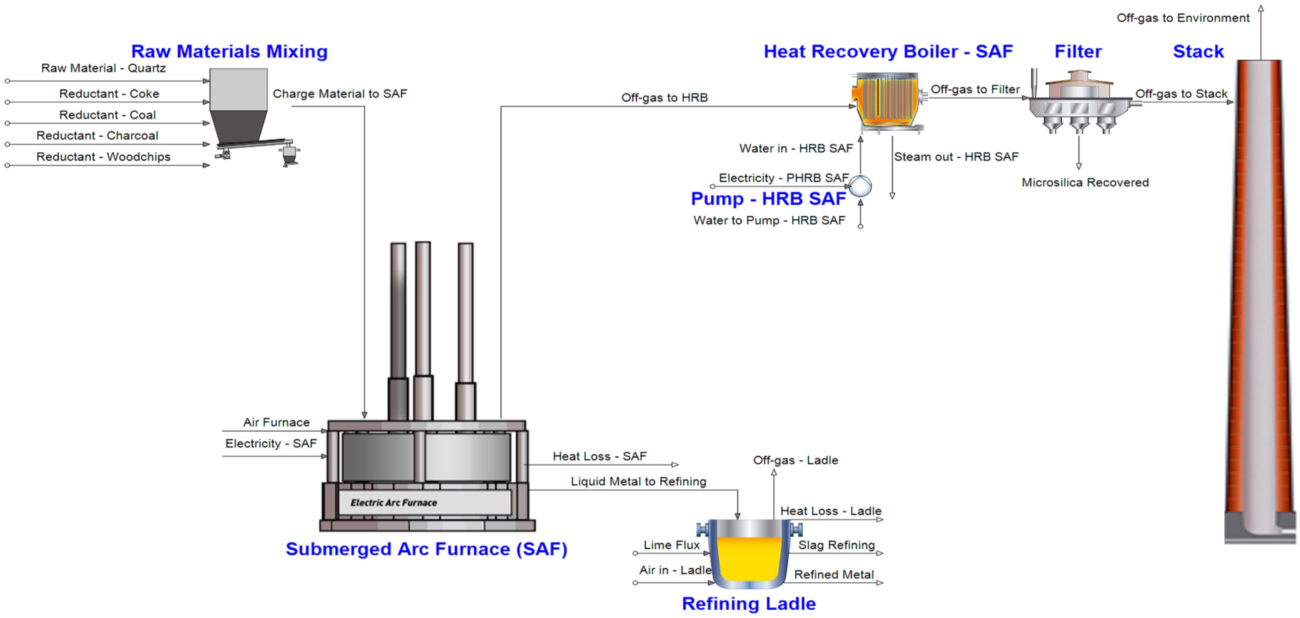

Figure C.1: Conventional silicon production (SAF) model. In HSC Chemistry. Modified from the models provided by HZDR[1].

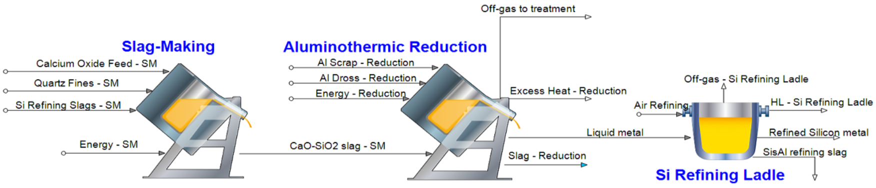

Figure C.2: SisAl process. Main production line. In HSC Chemistry. Modified from the models provided by HZDR[1].

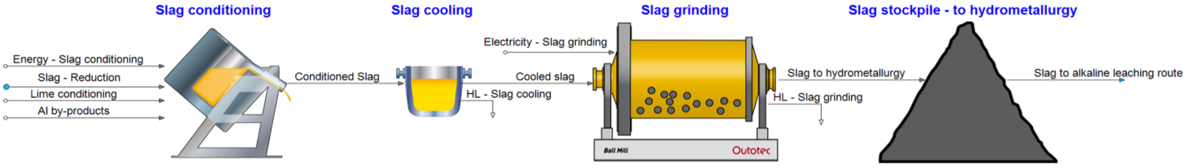

Figure C.3: SisAl process. Reduction of slag (from main production line). In HSC Chemistry. Modified from the models provided by HZDR[1].

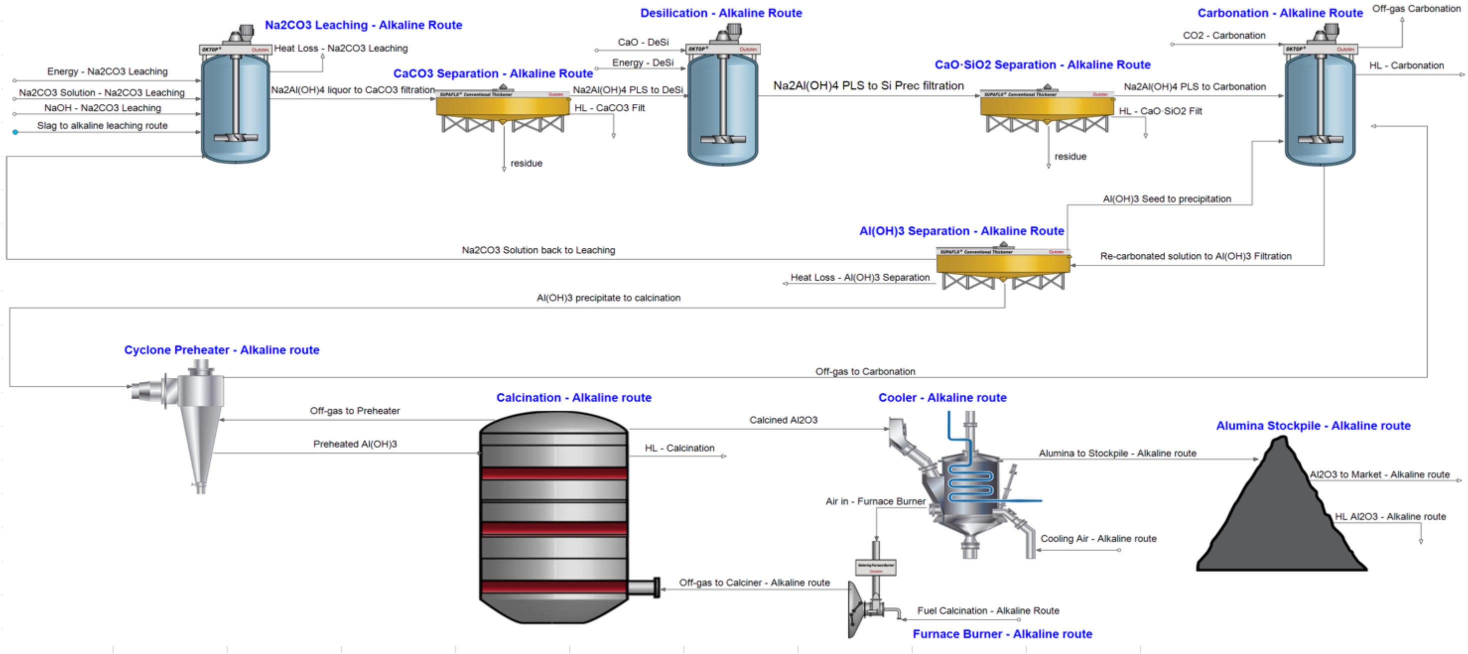

Figure C.4: SisAl process. Alkaline leaching route for the obtention of alumina. In HSC Chemistry. Modified from the models provided by HZDR[1].

Appendix D

LCIA results

Table D.1: Characterization results for the life cycle impact assessment. F.U.: 1 tonne of silicon after ladle refining in Norway.

Results for the different impact categories			
Impact	Units	Carbothermic Si	Aluminothermic Si
Global warming	kg $CO_{2\ eq.}$	6.269,02	5.149,63
Ozone formation, human health	kg $NOx_{eq.}$	27,12	5,68
Fine particulate matter formation	kg $PM_{2,5\ eq.}$	10,78	2,16
Ozone formation, terrestrial ecosystems	kg $NOx_{eq.}$	27,2	5,88
Terrestrial acidification	kg $SO_{2\ eq.}$	33,2	3,8
Freshwater eutrophication	kg $P_{eq.}$	2,35	0,57
Marine eutrophication	kg $N_{eq.}$	0,15	-5,2
Terrestrial ecotoxicity	kg 1,4-$DCB_{eq.}$	2.967,49	17.365,99
Freshwater ecotoxicity	kg 1,4-$DCB_{eq.}$	127,28	43,83
Marine ecotoxicity	kg 1,4-$DCB_{eq.}$	169,28	59,94
Human carcinogenic toxicity	kg 1,4-$DCB_{eq.}$	172,94	-538,98
Human non-carcinogenic toxicity	kg 1,4-$DCB_{eq.}$	2.577,62	2.029,92
Land use	m^2a $crop_{eq.}$	461,92	242,56
Mineral resource scarcity	kg $Cu_{eq.}$	4,21	-12,24
Fossil resource scarcity	kg $oil_{eq.}$	1.188,23	671,7

Table D.2: Normalised results for the life cycle impact assessment. F.U.: 1 tonne of silicon after ladle refining in Norway.

Normalised results for the different impact categories		
Impact	Carbothermic Si	Aluminothermic Si
Global warming	0,78	0,64
Ozone formation, human health	1,32	0,28
Fine particulate matter formation	0,42	0,08
Ozone formation, terrestrial ecosystems	1,53	0,33
Terrestrial acidification	0,81	0,09
Freshwater eutrophication	3,61	0,88
Marine eutrophication	0,03	-1,13
Terrestrial ecotoxicity	2,86	16,76
Freshwater ecotoxicity	103,73	35,72
Marine ecotoxicity	164,03	58,09
Human carcinogenic toxicity	62,43	-194,57
Human non-carcinogenic toxicity	17,3	13,62
Land use	0,07	0,04
Mineral resource scarcity	3,5E-05	-1,02E-04
Fossil resource scarcity	1,21	0,69

Table D.3: Contribution to endpoint categories. Damage assessment and weighting results.

Endpoint impacts			
Category	Unit	Carbothermic	Aluminothermic
Damage assessment			
Human health	DALY	1,42E-02	5,07E-03
Ecosystems	species.yr	3,45E-05	1,91E-05
Resources	USD2013	157,13	246,91
Normalised results			
Human health	–	0,6	0,213
Ecosystems	–	4,82E-02	2,66E-02
Resources	–	5,61E-03	8,81E-03
Weighting results			
Human health	Pt	239,86	85,31
Ecosystems		19,27	10,66
Resources		1,12	1,76
TOTAL		260,25	97,73

Table D.4: Contribution to the environmental impact per process (midpoints). Results expressed in % of normalised score. F.U.: 1 tonne of silicon after ladle refining in Norway.

Contribution to the impact results per process	
Carbothermic system	
Process emissions	1,15%
Carbon reductants	59,31%
Quicklime consumed	0,09%
Silica sand (input)	1,98%
Electricity	37,45%
Silica sand (recovered)	Negative
Final waste streams	0,03%
Aluminothermic system	
Process emissions	0,05%
Aluminium reductants	Negative
Quicklime consumed	4%
Silica sand (input)	1,21%
Aluminium oxide (refining)	37,16%
Carbon dioxide consumption	20,9%
Others	0,06%
Electricity	12,33%
Alumina by-product	Negative
Final waste streams	24,29%

Appendix E

Sensitivity analyses and scenarios results

Table E.1: Results for the sensitivity analysis (European electricity mix).

Sensitivity for electricity mix (results for European electricity mix)		
Impact	Carbothermic	Aluminothermic
Global warming (kg $CO_{2\ eq.}$)	11.711,27	7.965,93
Ozone formation, human health (kg $NOx_{eq.}$)	37,94	11,28
Fine particulate matter formation (kg $PM_{2,5\ eq.}$)	20,01	6,93
Ozone formation, terrestrial ecosystems (kg $NOx_{eq.}$)	38,1	11,52
Terrestrial acidification (kg $SO_{2\ eq.}$)	57,63	16,44
Freshwater eutrophication (kg $P_{eq.}$)	8,35	3,68
Marine eutrophication (kg $N_{eq.}$)	0,58	-4,98
Terrestrial ecotoxicity (kg 1,4-$DCB_{eq.}$)	6.980,78	19.442,83
Freshwater ecotoxicity (kg 1,4-$DCB_{eq.}$)	299,29	132,85
Marine ecotoxicity (kg 1,4-$DCB_{eq.}$)	407,47	183,21
Human carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	499,23	-370,12
Human non-carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	7.376,81	4.513,44
Land use (m^2a $crop_{eq.}$)	662,44	346,32
Mineral resource scarcity (kg $Cu_{eq.}$)	9,83	-9,32
Fossil resource scarcity (kg $oil_{eq.}$)	2.613,87	1.412,05

Table E.2: Results for the sensitivity analysis (post-consumer Al input).

Sensitivity for aluminium input (results for post-consumer Al input)	
Impact	Aluminothermic
Global warming (kg $CO_{2\ eq.}$)	9.152,51
Ozone formation, human health (kg $NOx_{eq.}$)	18,27
Fine particulate matter formation (kg $PM_{2,5\ eq.}$)	10,94
Ozone formation, terrestrial ecosystems (kg $NOx_{eq.}$)	18,74
Terrestrial acidification (kg $SO_{2\ eq.}$)	28,60
Freshwater eutrophication (kg $P_{eq.}$)	1,4
Marine eutrophication (kg $N_{eq.}$)	0,78
Terrestrial ecotoxicity (kg 1,4-$DCB_{eq.}$)	38.344,59
Freshwater ecotoxicity (kg 1,4-$DCB_{eq.}$)	217,36
Marine ecotoxicity (kg 1,4-$DCB_{eq.}$)	296,21
Human carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	-277,82
Human non-carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	5.753,19
Land use (m^2a $crop_{eq.}$)	1.271,64
Mineral resource scarcity (kg $Cu_{eq.}$)	13,9
Fossil resource scarcity (kg $oil_{eq.}$)	2.028,52

Table E.3: Results for the recirculation of materials scenario.

Sensitivity for aluminium input (results for the case of material recirculation)	
Impact	Aluminothermic
Global warming (kg $CO_{2\ eq.}$)	3.098,18
Ozone formation, human health (kg $NOx_{eq.}$)	3,29
Fine particulate matter formation (kg $PM_{2,5\ eq.}$)	0,65
Ozone formation, terrestrial ecosystems (kg $NOx_{eq.}$)	3,44
Terrestrial acidification (kg $SO_{2\ eq.}$)	-0,13
Freshwater eutrophication (kg $P_{eq.}$)	-0,06
Marine eutrophication (kg $N_{eq.}$)	-5,26
Terrestrial ecotoxicity (kg 1,4-$DCB_{eq.}$)	9.998,71
Freshwater ecotoxicity (kg 1,4-$DCB_{eq.}$)	-22,34
Marine ecotoxicity (kg 1,4-$DCB_{eq.}$)	-33,76
Human carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	-591,86
Human non-carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	-72,09
Land use (m^2a $crop_{eq.}$)	191,7
Mineral resource scarcity (kg $Cu_{eq.}$)	-17,61
Fossil resource scarcity (kg $oil_{eq.}$)	308,72

Table E.4: Biogenic emissions in the substitution of hard coal by charcoal (biogenic emissions from the use of woodchips are also included in this figure).

Percentage substitution	Hard coal	Charcoal	Biogenic emissions
0%	1,65 t	0 t	0,85 t
20%	1,32 t	0,33 t	1,85 t
40%	0,99 t	0,66 t	2,84 t
60%	0,66 t	0,99 t	3,84 t
80%	0,33 t	1,32 t	4,83 t
100%	0 t	1,65 t	5,81 t

Table E.5: Results for the complete substitution of hard coal by charcoal.

Scenario of 100% hard coal substitution	
Impact	Carbothermic using charcoal
Global warming (kg $CO_{2\ eq.}$)	3.391,73
Ozone formation, human health (kg $NOx_{eq.}$)	27,09
Fine particulate matter formation (kg $PM_{2,5\ eq.}$)	11,11
Ozone formation, terrestrial ecosystems (kg $NOx_{eq.}$)	28,29
Terrestrial acidification (kg $SO_{2\ eq.}$)	31,57
Freshwater eutrophication (kg $P_{eq.}$)	0,3
Marine eutrophication (kg $N_{eq.}$)	0,03
Terrestrial ecotoxicity (kg 1,4-$DCB_{eq.}$)	4.164,41
Freshwater ecotoxicity (kg 1,4-$DCB_{eq.}$)	68,54
Marine ecotoxicity (kg 1,4-$DCB_{eq.}$)	88,66
Human carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	46,55
Human non-carcinogenic toxicity (kg 1,4-$DCB_{eq.}$)	818,59
Land use (m^2a $crop_{eq.}$)	3.905,53
Mineral resource scarcity (kg $Cu_{eq.}$)	3,84
Fossil resource scarcity (kg $oil_{eq.}$)	282,21

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