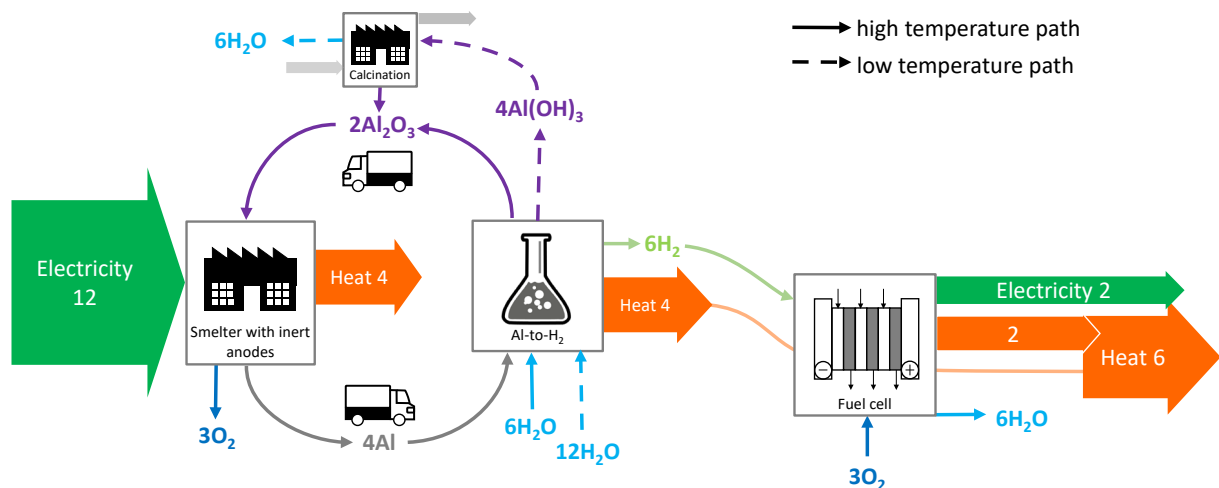




Final report dated 18.02.2022

AlEnCycles

Aluminium-Redox-Cycles for the Production of Heat and Electricity for Buildings based on Renewable Energies



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Swiss Federal Office of Energy SFOE
Energy Research and Cleantech Section
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Co-financing

Energie 360° AG
Aargauerstr. 182
Postfach 805
8010 Zürich
www.energie360.ch

Solenthaler Recycling AG
Moosburg
9200 Gossau – Switzerland
www.sorec.ch

Subsidy recipients:

SPF Institute for Solar Technology
Eastern Switzerland University of Applied Sciences (OST)
Oberseestr. 10, 8640 Rapperswil
www.spf.ch / www.ost.ch

Authors:

Michel Y. Haller, SPF, michel.haller@ost.ch
Dominik Amstad, SPF, dominik.amstad@ost.ch
Mihaela Dudita, SPF, mihaela.dudita@ost.ch
Yvonne Bäuerle, SPF, yvonne.baeuerle@ost.ch

SFOE project coordinators:

Andreas Eckmanns, andreas.eckmanns@bfe.admin.ch
Elimar Frank, elimar.frank@frank-energy.com
Stephan Mathez, stephan.a.mathez@solarcampus.ch

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Zusammenfassung

Im Rahmen des Projekts AlEnCycles wurde die Verwendung von Aluminiumschrott aus Recyclingströmen für die Erzeugung von Wärme und Wasserstoff untersucht. Die Vorteile dieses Konzepts sind die hohe Energiespeicherdichte ($23,6 \text{ MWh/m}^3$) von Aluminium als Energieträger, die Möglichkeit, überall und jederzeit Wärme und Strom zu erzeugen, sowie eine potenziell kostengünstige Quelle für Aluminium. Wärme und Wasserstoff wurden aus sieben verschiedenen Aluminiumschrottquellen erzeugt. Die Umwandlungseffizienz lag bei sechs der Proben nahe bei 100 %. Die Analyse der erhaltenen festen Reaktionsprodukte ergab, dass diese aufgrund bestimmter metallischer Verunreinigungen nicht direkt zur Kalzinierung und Herstellung von elementarem Aluminium in einem herkömmlichen Schmelzflussverfahren verwendet werden können. Um eine ökologisch und ökonomisch sinnvolle Lösung zu finden, müssten die Reaktionsprodukte aufbereitet und gereinigt oder in - derzeit nicht existierenden - Schmelzöfen verwendet werden, die nur für die Herstellung von Aluminium für energetische Zwecke bestimmt sind. Wenn jedoch eine Lösung für dieses Problem gefunden werden kann, hat das Konzept das Potenzial für eine saisonale Energiespeicherung mit Kosten in der Größenordnung von 9 €/cts/kWh, wobei die Kosten für den Energieeinsatz und die Kosten für die Umwandlung der gespeicherten Energie in Wärme und Wasserstoff oder Elektrizität nicht berücksichtigt sind. Nach der in diesem Projekt durchgeführten LCA-Analyse reduziert die Bereitstellung von Wärme und Strom für Gebäude aus Al-to-Energy das damit verbundene GWP je nach verfügbarem (erneuerbarem) Strommix um 33 – 80 % gegenüber einem Mini BHKW auf der Basis von Erdgas. Die große Bandbreite dieser GWP-Werte ist das Ergebnis unterschiedlicher Umweltbelastungen, die mit verschiedenen Technologien und Datensätzen für die Stromerzeugung aus erneuerbaren Energiequellen verbunden sind.

Summary

Within the AlEnCycles project, the use aluminium scrap from recycling streams for the production of heat and hydrogen was investigated. Advantages of this concept are the high energy storage density (23.6 MWh/m^3) of aluminium as an energy carrier, the possibility to produce heat and electricity anywhere, anytime, and a potential low-cost source of the aluminium. Heat and hydrogen was produced from seven different aluminium scrap sources. Conversion efficiency was close to 100 % for six of the samples. Analysis of the obtained solid reaction products showed that, due to the presence of certain metal impurities, the resulting reaction products cannot be used directly for calcination and production of elementary aluminium in a conventional smelter process. In order to reach an ecologically and economically viable solution, reaction products would have to be treated and purified or used in – currently not existing - smelters dedicated only for the production of aluminium for energetic purposes. However, if a solution for this problem can be found, the concept has the potential for seasonal energetic energy storage with cost in the range of 9 €/cts/kWh, excluding cost of energy input and cost for converting the stored energy into heat and hydrogen or electricity. According to the LCA analysis that was performed in this project, providing heat and electricity for buildings from Al-to-Energy units reduces GWP, depending on the available (renewable) electricity mix by 33-80% compared to a mini-CHP unit that is based on natural gas. The large range of these GWP value is a result of different environmental burdens associated with different technologies and datasets for renewable electricity production.



Main findings

- Different aluminium scrap sources can be converted to heat and hydrogen with high efficiency
- The concept of Al-to-Energy based on aluminium scrap can be economically advantageous, if the resulting oxidized aluminium can be put to use or recycled
- Levelized cost for seasonal energy storage of 9 €-cts/kWh seem to be possible with this approach
- Life cycle assessment shows significant advantages in terms of reduction of climate gas emissions compared to mini-CHP units that use natural gas
- The main influencing factor for the amount of GWP reduction that can be achieved is the electricity mix that is used for calcination and for the inert electrode Al smelting process
- Whether the Al stems from primary Al or from scrap is of minor importance for the reduction of GWP, and also minor losses of Al or NaOH with each energy cycle have no significant effect on the results



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Abbreviations

Al	Aluminium
Al(OH) ₃	Aluminium hydroxide
Al ₂ O ₃	Aluminium oxide
CHP	Combined Heat and Power
CNC	Computerized Numerical Control
DIN	Deutsche Industrienorm (German industry standard)
EMPA	Swiss Federal Laboratories for Materials, Science and Technology
EN	European standard
EOL	End Of Life
EU	European Union
GHG	Greenhouse Gas
GWP	Global Warming Potential
HHV	High Heating Value
ICP-OES	Inductively coupled plasma - optical emission spectrometry
IPCC	Intergovernmental Panel on Climate Change
LCA	Environmental Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LME	London Metal Exchange
LOI	Loss of Ignition
mt	metric tonne
PEM	Polymer Electrolyte Membrane
PV	Photovoltaic
RH	relative humidity
SEM	Scanning Electron Microscopy
UBCS	Used Beverage Cans Scrap
UMTEC	Institut für Umwelt- und Verfahrenstechnik der OST – Ostschweizer Fachhochschule
XRD	X-Ray Diffraction
XRF	X-ray fluorescence



1 Introduction

1.1 Background information and current situation

Storing large quantities of renewable energy over long periods is the most important unsolved problem of the Swiss Energy Strategy 2050.

Due to the phase out of nuclear power, heating oil and natural gas, new solutions are being sought to supply buildings with renewable electricity and heat. In the future. The use of E-mobility and heat pumps is increasing and although this will help to reduce fossil energy use and combat climate change, these technologies will compete for electricity in winter with industry, households and commerce. On the other hand, electricity production from wind, hydropower and photovoltaics is today less expensive than from fossil fuels or nuclear power. However, covering the energy demand in winter (heat and electricity) with local renewable energy is only possible in niches or would be associated with high costs, considering only the currently available technology.

"Renewable metal fuels" have great potential for storing renewable energy over long periods of time [1]. They offer a simple, safe and efficient solution for converting electrical energy into chemically stored energy. Using renewable metal fuels, heat and electricity can be cost-effectively supplied anytime, anywhere, and even in small units. Aluminium is the most promising candidate for a renewable metal fuel [2], in particular for decentralized heat and electricity production [3].

A seasonal energy storage based on the aluminium redox cycle (chemical reduction and oxidation of aluminium) was proposed in the HybridStock project (final report in publication). In this concept, electricity from solar or other renewable sources can be used to convert aluminium oxide or aluminium hydroxide or aluminium oxide to elementary aluminium ($\text{Al}^{3+} \rightarrow \text{Al}$). This is the charging process. In the discharging process, aluminium is oxidized ($\text{Al} \rightarrow \text{Al}^{3+}$), releasing hydrogen and heat. As a by-product, aluminium hydroxide is obtained in case of the low temperature path or aluminium oxide for the high temperature path. Hydrogen is further used in a fuel cell to produce electricity. The heat produced in the fuel cell and in the aluminium oxidation process can be used for domestic hot water production and space heating. Researchers from SPF have shown that the production of heat and electricity from aluminium is possible on a laboratory scale and can be realised with a high efficiency of more than 90%.

In July 2020, aluminium cost around 1600 CHF/t on the world market. With an efficiency of 90% for the conversion of the chemically stored energy to heat and electricity for buildings, useful energy may be produced with Al-fuel cost of 21 Rp/kWh. Aluminium from recycling streams reaches peak prices of 700 CHF/mt. This would enable electricity and heat to be produced at an energy carrier cost of 9 cents per kWh, which is competitive compared to other fuels.



1.2 Purpose of the project

The project AlEnCycles focuses on the use of aluminium redox processes as a means for seasonally storing renewable energy. Different sources for the energetic use of aluminium are identified and tested, including aluminium from recycling streams as well as unaltered or "new" aluminium of higher purity and better-defined composition. The project answers questions concerning the suitability of different aluminium sources and the implications that the source has on cost and environmental aspects.

1.3 Objectives

The primary aim is to compare the two basic materials, a) scrap or used aluminium and b) primary aluminium, for use in the production of heat and electricity in buildings in Switzerland.

Goals:

1. Suppliers and prices for different Al materials (new and scrap) will be identified;
2. Al-to-Energy for different Al materials from different suppliers will be tested at laboratory scale for conversion to hydrogen and heat; the materials will be characterized in terms of elementary composition and completeness of reaction;
3. The resulting solid products of the reaction with different Al materials will be examined in terms of composition and suitability for the use in other processes, including also the re-introduction into the Al production process (calcination and smelting);
4. Identification of possible customers and sales prices for large quantities of solid reaction products from the Al-to-Energy conversion process;
5. Comparison of energy cost and the reduction of global warming potential (GWP) resulting from the use of different Al materials (and material cycles) for the production of heat and electricity for buildings with other options for heat and electricity supply of buildings.

Detailed research questions to be answered:

6. Which Al materials can be used (new and scrap) for the production of heat and electricity in buildings, which are possible suppliers and at which cost could this material be obtained?
7. What are the implications of using different Al materials, especially concerning the resulting solid products of the reaction and their further use or market value?
8. Which are possible further uses of the solid reaction products, depending on their purity, i.e. depending on the Al material used for the reaction?
9. What are the financial and ecological consequences of using different Al materials? Which options are a) financially viable and b) environmentally advantageous?



2 Procedures and methodology

2.1 Aluminium sources, pre-treatment and analysis

Two types of aluminium categories were investigated as input sources for aluminium energy cycles in Switzerland:

- a) scrap or used aluminium;
- b) primary aluminium.

Corresponding aluminium sources for the production of heat and hydrogen were identified together with the industrial partners and are listed in Table 2.1 and shown in Figure 2.1.

Except for the pure aluminium sample (no. 8), all samples contained different impurities, e.g. coffee leftovers, oils, surfactants and other metals, and were thus cleaned before use.

Table 2.1: Aluminium samples chosen for the AlEnCycles project.

Sample	Source	Description
1	Nestlé Nespresso SA	Shredded capsules with coffee impurities
2	Nestlé Nespresso SA	Large capsules with coffee impurities
3	Nestlé Nespresso SA	Coffee capsules and pads with coffee impurities
4	Nestlé Nespresso SA	Waste from coffee pad production
5	Solenthaler Recycling AG	Used beverage cans from aluminium recycling stream
6	Solenthaler Recycling AG	Wet, aluminium chips from machining in industry
7	Solenthaler Recycling AG	Dry, small aluminium chips from precision machining in industry (e.g. turning lathe)
8	Aluminium Laufen AG	Aluminium block, pure aluminium (class P1020)



Figure 2.1: Visual aspect of the aluminium samples as obtained from the partners (Sample 1 to 8), before treatment.



As the raw materials had different size, as well as different impurities, e.g. coffee leftovers, oils, surfactants, before performing any investigations, they were pre-treated following the steps described below.

2.1.1 Preparation of coffee capsules for removing the coffee impurities

Samples 1 to 3 (Table 2.1) had to be washed with water to remove the coffee leftovers. Sample 2 and 3 were first shredded with the larger shredder from UMTEC (Figure 2.2) in order to make the pieces smaller and open up the capsules, so that they can be washed better. After that, the material from each sample was put into a large bucket, which was filled with water. During this process, water was shot with a high-pressure cleaner into the bucket in order to mix very well the capsules and wash them. This process was repeated approximately five times for the sample 2, until the washing water was clear. For sample 1 and 3, this process was repeated approx. ten times. After each washing step, a sieve was used to separate the sample and the water. In this process, not only the coffee particles were removed, but also small plastic particles. This was especially the case for sample 3 that contained visibly more plastic material. Thus, the organic content in this sample was slightly reduced.



a)



b)

Figure 2.2: Sample 3 before pre-treatment, with waste coffee particles (a) and the shredder used to reduce the size of Sample 2 and 3 before washing (b).

Although the shredder, which is normally used for shredding aluminium cans, was cleaned before usage, it is still possible that some contamination with particles that might have remained inside the shredder has occurred.



Figure 2.3: Sieve with sample 1.



Figure 2.4: Sample 1 pre-washing.

2.1.2 Cutting and shredding

The solid aluminium block (Sample 8) was cut into long chips in the mechanical workshop using a CNC milling machine. Capsules (Sample 1 to 3, after removal of impurities) and chips of sample 8 were cut into smaller pieces with a commercial blender (Blendtec Xpress) and then sieved with 5 mm holes. Material that did not pass the sieve was discarded.

2.1.3 Cleaning and drying

After pre-washing and shredding as described in 2.1.1 and 2.1.2, all the samples were washed in buckets with water ($\sim 55^{\circ}\text{C}$) 2-4 times. After that, they were washed with demineralized water (conductivity $< 15 \mu\text{S/cm}$), introduced into laundry bags and dried in a climatic chamber (CTS, model CL-40/350/S) at 80°C and 10 % RH until mass was constant. The aspect of the samples after this pre-treatment step is shown in Figure 2.5.



Figure 2.5: Visual aspect of the aluminium samples after cleaning and drying.



2.1.4 Thermal treatment

After cleaning and drying, all samples were thermally treated at 550°C for 30 minutes according to the standard procedure from DIN EN 15935:2012 ("Sludge, treated bio-waste, soil and waste - Determination of loss on ignition"). Using this method, the organic matter content can be evaluated by calculating the mass loss. The remaining dry mass can be associated with the presence of metal and/or metal oxide (s). Metal oxides are also formed during the thermal treatment, thus this method cannot distinguish between metals and metal oxides.

2.1.5 Chemical composition

The elemental composition of the thermally treated material (see Section 2.1.4) was evaluated by ICP-OES with a Thermo iCAP 6300 from Thermo Scientific (detection capability <1 ppb), using a multi element standard which allows for the simultaneous detection of 23 elements: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, Zn. For ICP-OES, ca. 250 mg of samples were dissolved in 5 mL HCl, 2 mL of HNO₃ and 10 mL of H₂O and then microwave digested using a MLS Ethos 1 digester. For all eight thermally treated samples, the aluminium content was evaluated as well as the presence of the elements mentioned above.

2.2 Conversion to heat and hydrogen

2.2.1 Efficiency and kinetics of the reaction

To assess the completeness of reaction, the ANKOM^{RF} Gas Production System was used. This system derives the produced gas volume from the pressure increase in a closed bottle system with defined content of liquid and gas volume. The main components are:

- 1) glass bottles 1000 mL;
- 2) modules for pressure monitoring (ANKOM^{RF} Gas Production System);
- 3) reference module zero (ambient pressure);
- 4) data acquisition system.

The ANKOM glass bottles coated with a polymeric film for safety reasons in case that more pressure is produced than anticipated and a glass would break. Aluminium samples that were washed and dried according to section 2.1.3 (Figure 2.5) were inserted within a capsule that dissolves in the aqueous NaOH solution and thus prevents that the reaction starts before the bottle is closed.

As a reaction promoter, 200 mL of 6 M NaOH_(aq) solution was chosen, considering results of the optimization process from the previous project HybridStock [4]. The solution was prepared from a concentrated NaOH solution (50 wt. %, Sigma Aldrich lot #STBH9704, code 415413-4L, density 1.515 g/mL at 25°C).

In addition to the eight samples described in section 2.1, a reference Al sample was used (aluminium grit, Merck, code 8149171000, purity ≥ 99.0 %, density 2.7 g/cm³ at 25 °C).

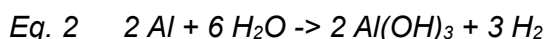


Except for the pure aluminium and the reference sample (Samples no. 8 and 0), all the other samples originally contained different impurities, e.g. coffee leftovers, oils, surfactants and other metals. These were removed as much as possible by the pre-treatment described in section 2.1.

The pressure increase that was delivered in psi by the ANKOM system was converted to SI units. For the calculation of the produced amount of gas, Eq. 1 was used, where p is the pressure (expressed in kPa), V is the gas volume (expressed in L), T is the gas temperature (in K) and $R = 8.314 \text{ L}\cdot\text{kPa} / (\text{K}\cdot\text{mol})$ is the gas constant, and $V_\mu = 22.4 \text{ L/mol}$ is the molar volume of the gas.

$$\text{Eq. 1} \quad V_{H_2} = \frac{p \cdot V}{R \cdot T} \cdot V_\mu$$

The gas volume in the 1 L glass bottles was calculated considering the 200 mL of NaOH solution to promote the reaction. The maximum amount of hydrogen that can be produced from the aluminium that is contained in the Al sample was calculated according to Eq. 3.



Internal investigations at UMTEC have shown that the uncertainty of the determination of gas production with the ANKOM system is $\pm 4,2\%$.

Since pressure increase is registered over time, conclusions on the kinetics of the reaction can also be drawn.

2.2.2 Preparation and analysis of solid reaction products

To obtain enough solid reaction products (i.e. aluminium hydroxide) for chemical analysis, samples of 120 g from the pre-treated eight samples were used (Figure 2.5). The material was washed and dried according to 2.1.3 (no additional thermal treatment was applied). The samples were converted to aluminium hydroxide and hydrogen in Berzelius glass reactors with Graham condensers for recovery of water and sodium hydroxide vapours.

The aqueous solution was 500 mL of 6 M NaOH, and samples were introduced slowly (about 1 g sample per step). The temperature within the reactors were measured with a temperature sensor and the reactors were immersed into a thermostatic bath (Lauda Bath Alpha RA 24) that was set to keep the temperature in the range of 60-70 °C. For some of the fast reacting samples, temperature temporarily increased above this range. Before precipitation of solids started, a magnetic stirring system was used. After a certain amount of solid reaction products was formed, the magnetic stirring system was replaced with vertical, manual stirring.

At the end of the experiments, magnetic particles were collected from the magnetic stirrer and removed from the samples. After this, solid products were separated using a vacuum filtration system with the following specifications:

- vacuum pump (VWR, diaphragm vacuum pump, model VP 820);
- Büchner funnel;
- filter paper (Whatman, $\Phi 150 \text{ mm}$, 4-7 μm from Schleicher & Schuell).

After filtration, the solid reaction products were washed until the pH of the filtrate decreased from 14 to 7, which was checked with pH paper. During this process that was assisted by the vacuum pump, plastic impurities that accumulated at the top of the samples were removed.



Vacuum filtration also had a partial drying effect. After this process, samples were removed from the filter and let to fully dry at room temperature. During this process, most of the samples agglomerated (see Figure 2.6) and had to be broken down to a powder using a mortar and pestle. For Sample 8 and the reference sample 0, no crushing and grinding was necessary, since the resulting sample after drying was already a well-dispersed fine powder. If visible plastic or other non-crushable impurities (see Figure 2.6, right) were present, these were manually removed using different plastic and stainless steel sieves (wire mesh down to 10 micron).



Figure 2.6: Solid reaction products after washing and filtration / drying. Left: S6 with unreacted metal impurities visible, middle: S8 from "pure" Al, and right: plastic impurities together with aluminium hydroxide in S4.

Additionally to the nine samples introduced before, a sample from the project HybridStock that was obtained in the 400 Watt reactor system from aluminium grit was also included for further analysis (Sample 2M-R). This sample was obtained from a recycling metal grit and has only been filtered, but not washed or rinsed. It thus includes a high quantity of sodium hydroxide. More details about sample 2M-R can be found in the HybridStock report [5]. The aspect of the samples after washing, drying, grinding and manual removal of impurities is shown in Figure 2.7.



Figure 2.7: Aluminium-hydroxide samples prepared from Al-water reactions.



Surface morphology of the synthesized materials was analysed with scanning electron microscopy (SEM) using TESCAN VEGA3 (TESCAN instruments 41). These investigations were performed at the laboratory for High Performance Ceramics from EMPA in Dübendorf, Switzerland.

The crystalline phases of dried materials were characterized by X-ray diffraction (XRD) using a Bruker D2 Phaser ($\text{Cu K}\alpha_1$ radiation, $1.5406 \text{ \AA}$). The scans were collected in the 2θ range of $10\text{--}80^\circ$ with a step size of 0.02° .

A set of aluminium hydroxide samples (around 100 g per sample) was sent to TRIMET Aluminium SE for elemental investigations by X-ray fluorescence. The elemental composition of these solid reaction products (Section 2.2.2) was analysed by Terrachem GmbH (Mannheim, Germany). A high performance wavelength dispersive XRF spectrometer (Bruker AXS, Tiger S8) was used. The typical limit of detection of XRF ranges between 10 and 50 mg/kg (10-50 ppm). Samples were dried for at least 12 h at 105°C before measurements and then measured according to DIN 51001:2003-08. Elements with atomic number $Z=11$ (sodium) until $Z=92$ (uranium) were investigated. Additionally, the samples were thermally treated at 1050°C for minimum 1 h. The mass loss was recorded and reported as loss of ignition (LOI).

2.3 Global Warming Potential (GWP) and energy cost

A literature research on primary and secondary aluminium production was conducted and valuable background information on current processes and developments could be gathered. The corresponding aluminium material flow of these processes were established and graphically displayed to be able to determine the system boundaries of the Al-to-Energy process concept, both for the use case of primary and secondary aluminium as the source material.

Additionally, aluminium-recycling pathways were identified and are part of further discussions because the recycled aluminium represent a major share of the aluminium production today and in the future.

The potential environmental advantages of the Al-to-Energy process is evaluated using the standardized procedures of a LCA according to ISO 14040 [6] and ISO 14044 [7], which determines the environmental impact associated with the concept from resource extraction to end-of-life burdens. The presented attributional LCA includes a goal and scope definition, a Life Cycle Inventory (LCI) collection, a Life Cycle Impact Assessment (LCIA) and the interpretation of the results. The functional unit was defined to present 1 MJ of energy produced. It is important to note, that this functional unit contains a specific amount of heat and hydrogen or heat and electricity, depending on the system setup applied (without or with a fuel cell system).

Additionally, the overall cradle-to-grave LCA results are compared to other alternative Combined Heat and Power (CHP) technologies suitable for the installation in residential buildings. The analysis uses SimaPro 8.5.0.0 and the Ecoinvent database version 3.1. For this study, life-cycle GHG emissions and their associated impacts on climate change are used as



main indicators for the environmental performance of the process. All Greenhouse Gas (GHG) emissions are assessed by the IPCC 2013 GWP 100a V1.03 method.

The geographic coverage of this LCA is Switzerland and the EU-27 countries, and the time for the introduction of Al-to-Energy into the market is 2030. This means that today neither the Al-to-Energy unit nor the inert electrode aluminium smelting have reached commercial phase and thus, there is a lack of data on these technologies that is filled with best approximations according to expert's opinion.



3 Results and discussions

3.1 Aluminium sources, pre-treatment and analysis

3.1.1 Samples after pre-treatment

The pre-treatment included reducing sample size, cleaning (washing with water) and drying (see details in section 2.1). For the elemental analysis via ICP-OES, the organic impurities were removed using thermal treatment at 550 °C as described in section 2.1.4. Figure 3.1 shows the resulting materials after the pre-treatment process (washing and drying), and thermal treatment.

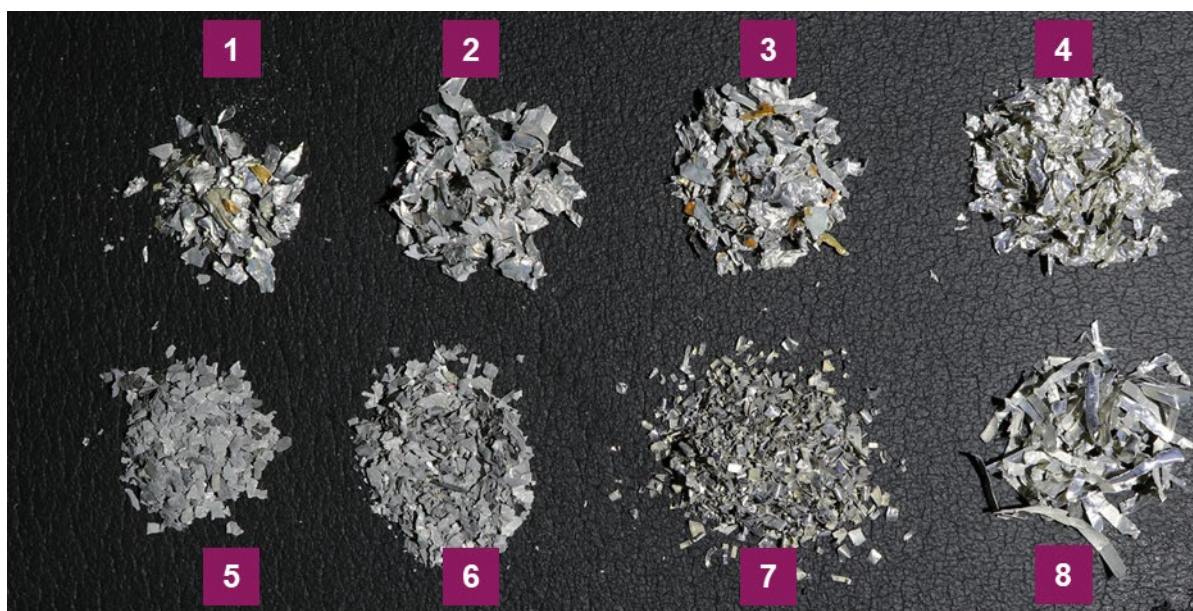


Figure 3.1: Aspect of the samples after washing, drying and thermal treatment.

3.1.2 Chemical analysis of cleaned and thermally treated input material

The relative mass loss observed after thermal treatment is shown in Figure 3.2. Mass loss is presumably organic matter that is converted mostly to $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$.

Although samples 1 to 4 are all from the production and/or use different kinds of coffee capsules and pads, there are notable differences. Whereas for samples 1 – 3, the mass loss of the samples after thermal treatment is between 10 and 20% (w/w), for sample 4 the mass loss is much higher (37%). Most likely, samples 1 to 4 included a rather high content of organic matter (11% for Sample 1, 19% for Sample 2, 14% for Sample 3 and 37% for Sample 4). All other samples only show minor mass loss of 0-2%, and thus low organic content. As expected, for sample 8, which is pure aluminium, no mass loss was detectable. Also sample 6, which was obtained from larger chips of industrial processing of aluminium, shows no detectable mass loss. Aluminium cans (sample 5) show a mass loss of 2%, and small chips from aluminium fine processing a loss of 1%. Details of the results from thermal treatment are shown in Table 3.1.

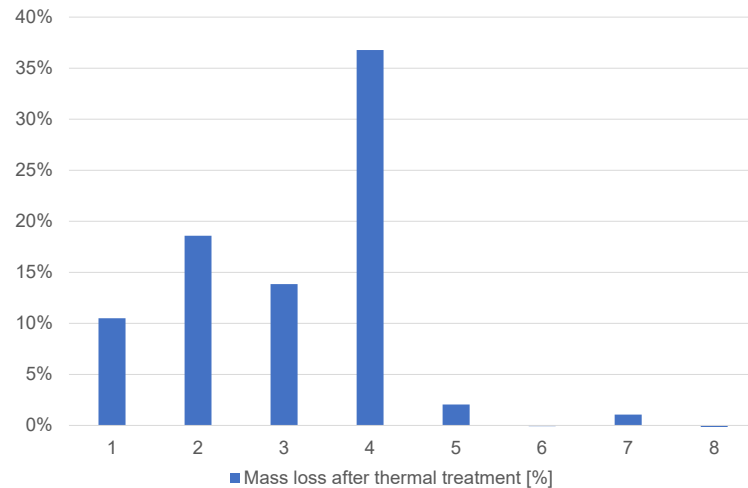


Figure 3.2: Fraction of mass lost after thermal treatment at 550°C according to DIN EN 15935:2012.

Table 3.1: Results from thermal treatment at 550°C according to DIN EN 15935:2012.

Sample	m ₀ [g]	m ₁ [g]	m ₂ [g]	Mass loss [g]	Mass loss [%]	Final mass [g]	Final mass [%]
1	76.510	1.514	77.865	0.159	11%	1.355	89%
2	71.602	1.592	72.898	0.296	19%	1.296	81%
3	71.420	1.524	72.733	0.211	14%	1.313	86%
4	70.656	1.468	71.584	0.540	37%	0.928	63%
5	69.953	1.554	71.475	0.032	2%	1.522	98%
6	71.288	1.566	72.855	-0.001	0%	1.567	100%
7	75.809	1.589	77.381	0.017	1%	1.572	99%
8	70.432	1.516	71.954	-0.006	0%	1.522	100%

m_0 is the mass of the crucible after heating empty at 550°C for 30 min; m_1 is the mass of the sample before thermal treatment; m_2 is the mass of the sample and crucible after heating at 550°C for 30 min; mass loss is calculated as $(m_0+m_1)-m_2$.

After thermal treatment, samples were digested as described in section 2.1.5 and the presence of metal elements was analysed with ICP-OES. Results of the ICP-OES analysis are shown in Figure 3.3 and Table 3.2.

From the scanned elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, Zn), only those with concentration higher than 0.1 mg/L (0.1 ppm) are shown. Depending on the sample, different metal impurities were found: Mg, Fe, Mn, Zn, Cu, Co, Cr and Ni. All samples contain iron in different concentration (Figure 3.3, Table 3.2), except for the pure aluminium sample (Sample 8) – in this case, the iron amount was lower than 0.1 mg/L. For Sample 1 to 4, only iron was detected (ranging from 0.7% in case of Sample 1 to 1% in



case of Sample 4). Sample 5 and Sample 6 contain many different metal impurities, the highest content being recorded for iron (4% for Sample 5, 11% for Sample 6). It is interesting to note that zinc was found only in Sample 6 (approx. 2%). Considering the reaction promoter used in this study (NaOH), only zinc reacts with NaOH (and H₂O) already at room temperature to release hydrogen gas [8]. However, also elemental impurities of Mg, Fe, Mn, Zn, Cu, Cr and Ni can lead to hydrogen formation when the reaction temperature is higher than 80°C.

Combining the results from Table 3.1 (thermal treatment) and Table 3.2 (ICP-OES), the purity of the original samples in terms of aluminium content was evaluated as presented in Table 3.3.

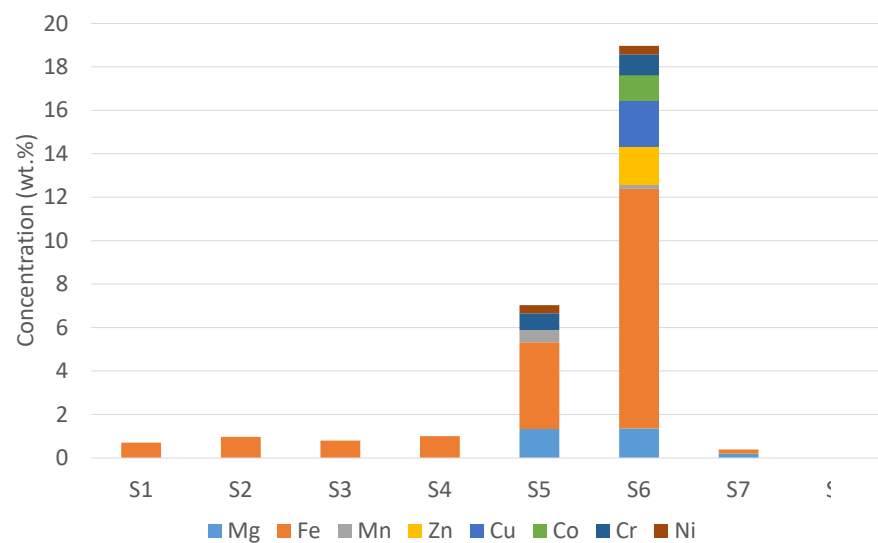


Figure 3.3: Results of the ICP-OES measurement showing the metallic impurities identified in the samples after thermal treatment (without aluminium).

Table 3.2: ICP-OES results indicating the aluminium content and the presence of different metal impurities.

Sample	Al		Other metal impurities [mg/L]							
	mg/L	% ^{a)}	Mg	Fe	Cu	Co	Cr	Mn	Ni	Zn
1	4.0	93.3	0	0.03	0	0	0	0	0	0
2	5.0	97.6	0	0.05	0	0	0	0	0	0
3	4.9	97.1	0	0.04	0	0	0	0	0	0
4	5.0	99.6	0	0.05	0	0	0	0	0	0
5	4.7	88.6	0.07	0.21	0	0	0.04	0.03	0.02	0
6	3.4	65.8	0.07	0.57	0.11	0.06	0.05	0.01	0.02	0.09
7	4.9	94.2	0.01	0.01	0	0	0	0	0	0
8	5.3	99.7	0	0	0	0	0	0	0	0

a) with respect to the mass of the (thermally treated) sample that was digested.



Table 3.3: Aluminium content of samples before thermal treatment.

Sample	1	2	3	4	5	6	7	8
Purity [%]	84	79	84	63	87	66	93	100

3.2 Conversion to heat and hydrogen

Based on the ANKOM analytical system that measures the increase of pressure in the overhead of the aqueous solution where the hydrogen evolving reaction(s) take place, the amount of hydrogen produced was calculated and compared to the amount that would be expected if all Al contained in the sample reacts completely. This ratio is given as R_{Al} in Table 3.4. Apparently, very pure samples such as sample 8 produced between 99 -100% of the expected amount. However, samples with other metallic impurities mostly produced more hydrogen than could be expected from the Al content of the sample. This is particularly striking for sample 6 that reached 142% of the theoretical value, and is no surprise, since metals other than aluminium may also react with water and produce hydrogen [8].

For this reason, the hydrogen production capacity when forming hydroxides in aqueous solution has been calculated based for all other metals too, based on the assumption that $M(OH)_3$ is formed for Cr, and $M(OH)_2$ for the other metals. A comparison of the hydrogen yield with this new theoretical maximum results in recoveries R_{Al+imp} between 95 – 105% for most of the samples. The only exceptions are sample 5 (beverage cans) where only 89.4% was reached, and sample 6 (shavings from machining in industry) that reached now 105.7% instead of 142% when impurities are not considered.

Table 3.4: Summary of the results obtained from completeness of reaction experiments.

No.	m_s [mg]	p %	m_{Al} [mg]	t [min]	R_{Al} %	Impurities	R_{Al+imp} [%]
1	401	83.5	335.0	420	104.5%	Mg Fe Mn Si Zn Cu Ti Cr Ni	103.5%
2	401.2	79.4	318.7	701	103.4%	Fe Mn Si Zn Cu Ti Cr Ni	101.8%
3	401.2	83.7	335.8	287	102.1%	Fe Mn Si Zn Cu Ni	100.8%
4	400.2	62.9	251.9	1276	99.2%	Fe Mn Si Zn Cu Ni	97.6%
5	401.9	86.7	348.6	337	103.4%	Mg Fe Mn Si Ca Zn Cu Ti Cr Ni	89.4%
6	401.5	65.8	264.0	131	142.2%	Mg Fe Mn Si Ca Zn Cu Cr Ni	105.7%
7	430.1	93.2	400.7	67	104.7%	Mg Fe Mn Si Ca Zn Cu Ni	103.6%
8	401.7	99.7	400.5	89	99.7%	Fe Si Cu Ni	99.7%

No. = sample number; m_s = amount of sample; p = purity of sample; m_{Al} = amount of Al contained in the sample; t = time to reach max. gas pressure; R = theoretical recovery rate if all gas produced were hydrogen produced from Al-water reaction of contained in the sample; Impurities = metallic impurities present in the sample.



In the Figure 3.4, the evolution over time of the ratio between the hydrogen volume and the maximum hydrogen volume obtained during the experiment is shown for all eight investigated samples. It is important to note that the experiments were performed at temperatures close to room temperature, i.e. 21°C to 25°C, and the reaction rates would be much higher at higher temperatures. Whereas the reaction of the pure samples 7 and 8 take place within about an hour at these temperatures, large coffee capsules and capsules matrix foil need longer to react and reaction of these samples took up to 8 hours.

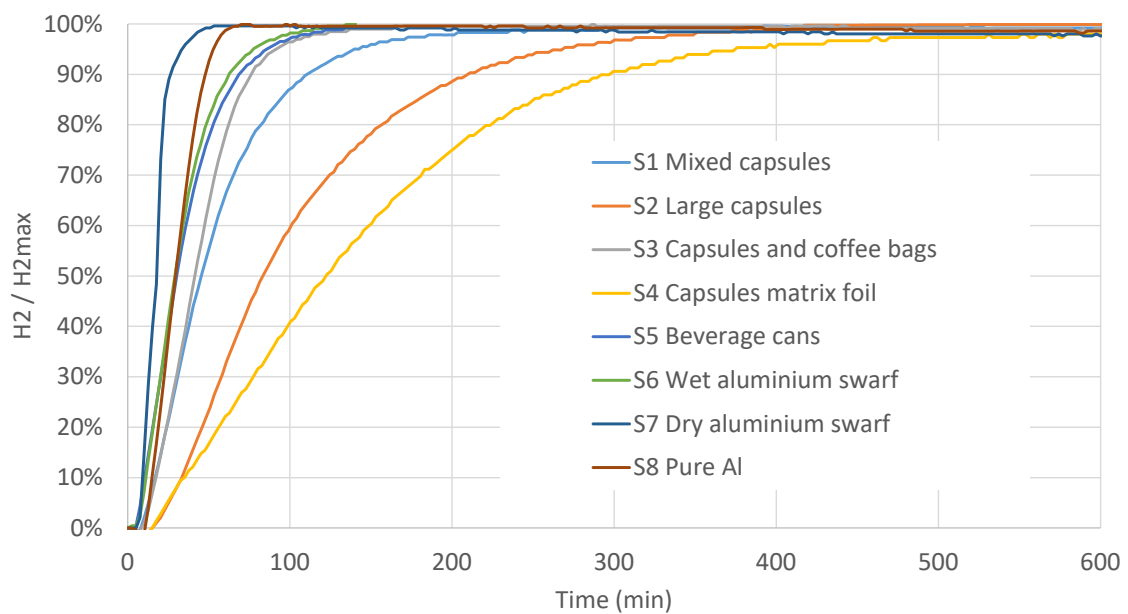


Figure 3.4: Hydrogen volume evolution expressed as the ratio between the volume at a specific time during the experiment and the maximum reached during the experiment.



3.3 Analysis of solid reaction products

3.3.1 Scanning electron microscopy

The surface morphology of the materials prepared as described in section 2.2.2 was analysed by scanning electron microscopy (SEM). Results are shown in Figure 3.5. Although the Al sources were in terms of composition and surface properties very different, all samples from the conversion experiments have a similar plate-like morphology. Platelets have different sizes, but usually a few microns wide and their thickness is less than 200 nm. The platelets are clustered together to show a “flower-like” morphology.

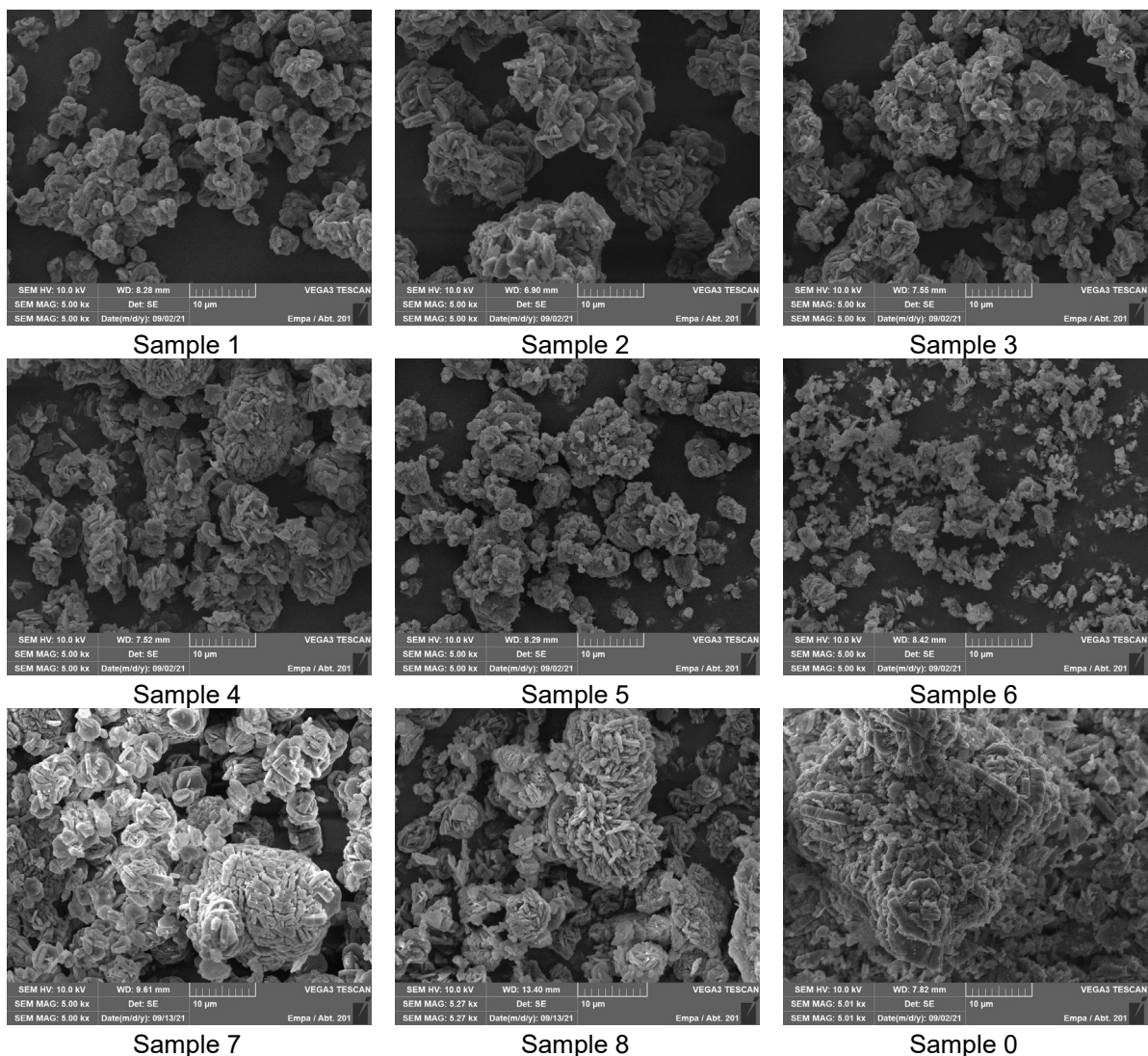


Figure 3.5: Surface morphology of the aluminium-hydroxide samples obtained by aluminium-water reactions from different Al-source scrap (Sample 1 to 7) and pure (Sample 8 and 0).



3.3.2 X-ray diffraction (XRD)

The crystalline phases in the aluminium-hydroxide materials were determined using XRD and the X-Ray patterns are shown in Figure 3.6. The X-ray diffraction pattern indicates for all samples the presence of the crystalline phase aluminium hydroxide $\text{Al}(\text{OH})_3$ (gibbsite form). This is in agreement with literature and with the previous experiments performed in the project HybridStock.

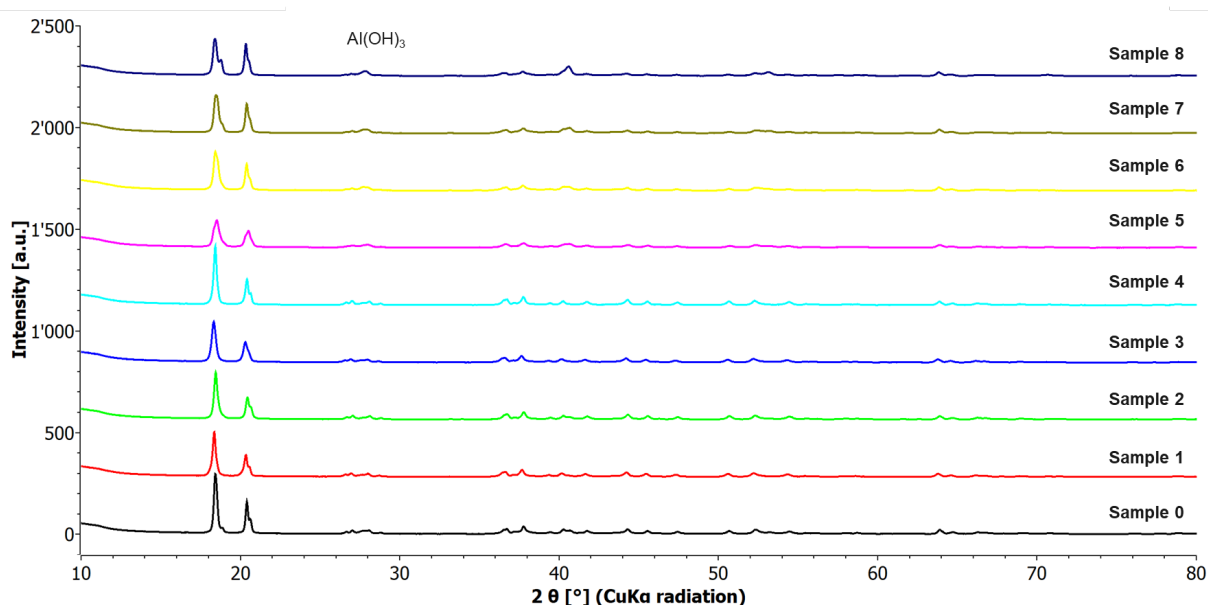


Figure 3.6: X-Ray patterns for the $\text{Al}(\text{OH})_3$ samples obtained from Al-water reaction dried at room temperature (no thermal treatment).

3.3.3 X-ray fluorescence

Results of the XRF analysis of aluminium hydroxide samples (after 12 h drying at 105 °C) are shown in Table 3.5 and Figure 3.7. It can be seen that considerable amounts of sodium (Na_2O) are found in all samples with concentrations mostly below 2% (wt/wt after subtraction of ignition losses (LOI)). The sample from the project HybridStock (2M-R) contains much more sodium (>7%), since it was not rinsed and neutralized as extensively as the examples from this project. Most samples contain considerable amounts of iron, some also magnesium and, to a lesser extent, also manganese, silicon and zinc were detected. The implications of these findings on the usability of the aluminium hydroxide or derived calcined products are discussed in section 3.5.2. The amounts of sodium present in the aluminium hydroxide indicate that about 6-10% of NaOH ends up in the aluminium hydroxide compared to the amount present in the quantity of water needed for the reaction, for samples that were rinsed to neutral pH, i.e. excluding sample 2M-R from HybridStock.

The mass loss (loss of ignition, LOI) is mainly due to the loss of H_2O and CO_2 , F, Cl, S as SO_2 , and also Na. A mass increase can also occur due to oxidation (e.g. formation of Fe_2O_3 from FeO).



Table 3.5: Weight fraction (%) of the chemical investigation for the solid reaction products obtained in the conversion of Al to hydrogen and Al(OH)₃ when using different recycling Al (S1 to S7) samples and pure aluminium (S8, S0), as well as a sample from the project Hybrid Stock (2M-R).

	S1	S2	S3	S4	S5	S6	S7	S8	S0	2M-R
Al ₂ O ₃	62	63.17	63.45	62.55	61.27	60.83	63.94	64.14	67.3	60.49
Na ₂ O	0.89	0.78	1.00	1.00	1.03	1.13	1.01	1.07	1.33	5.1
MgO	0.75				1.53	1.51	0.26			0.77
Fe ₂ O ₃	0.63	0.97	0.85	0.86	0.5	0.45	0.18	0.09	0.12	0.41
MnO	0.47	0.03	0.01	0.01	0.52	0.25	0.03			0.47
SiO ₂	0.31	0.07	0.05	0.04	0.31	0.84	0.09	0.03	0.04	0.35
CaO					0.1	0.02	0.02		0.02	0.03
ZnO	0.04	0.01	0.01	0.01	0.05	0.34	0.02		0.01	0.13
CuO	0.07	0.06	0.01	0.01	0.07	0.09	0.05	0.03		0.17
TiO ₂	0.03	0.05			0.06					0.04
Cr ₂ O ₃	0.01				0.02	0.09				
NiO	0.01	0.01	0.01	0.01	0.02	0.03	0.01	0.01		0.03
LOI*	34.78	34.86	34.61	34.52	34.53	34.42	34.39	34.63	34.13	32.02

* Loss of ignition (LOI) refers to the material loss during thermal treatment at 1050°C for 1h. The remaining dry mass can be associated with the presence of metal oxides.

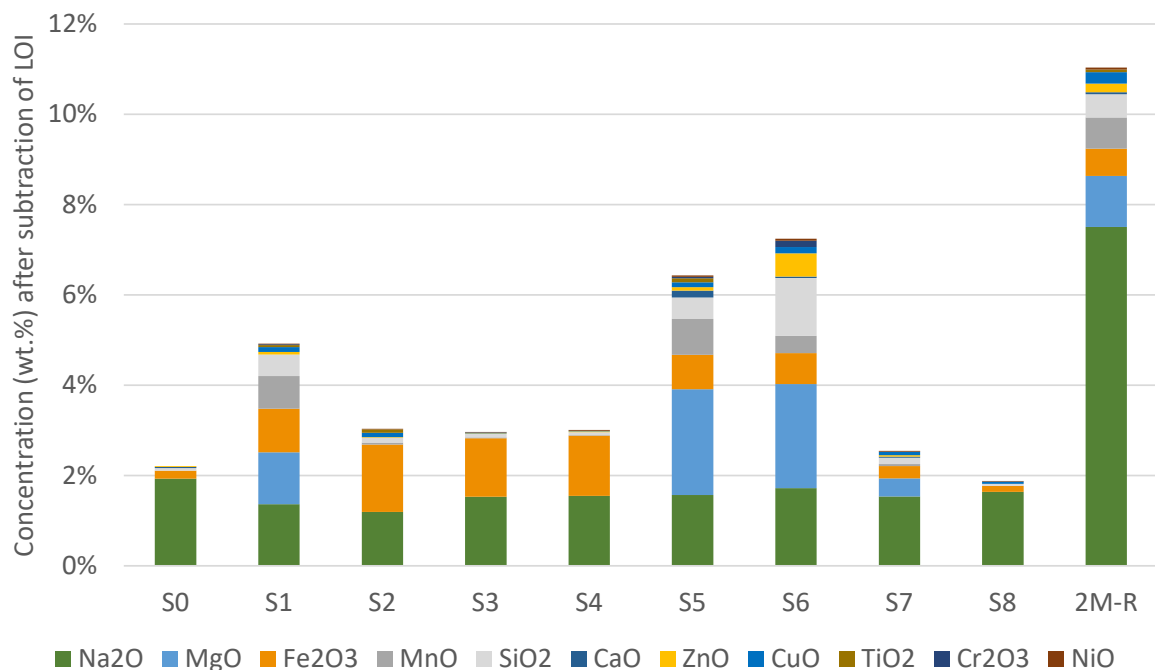


Figure 3.7: Concentrations (%wt) of different minerals given as mineral oxides in the aluminium hydroxide samples after subtraction of LOI (loss of ignition).



3.4 Comparison of GWP and energy cost

3.4.1 Introduction

Results of the detailed LCA analysis are summarized in this chapter. Figure 3.8 presents the general aluminium material flow of the global market, and additionally the new processes and material flows that would be introduced by using scrap or recycling aluminium for the production of energy.

In general, a recycling process can be described depending on the use case of the recycled material by: a) closed loop recycling, b) open loop recycling with down cycling, and c) open loop recycling without down cycling (semi-closed loop). For closed loop recycling, the flow of the recycled material leads into the same production system for new material. In this case, the material properties are not changed. In the EU, the recycling of aluminium beverage cans is based on such a closed-recycling loop. Open loop recycling, on the other hand, describes a process where the recycled material flows into another production system, i.e. resulting in different materials to be produced. It should be noted that the general Al scrap material flow will be influenced if a significant amount of Al scrap is used in the Al-to-Energy cycle. Thus, the Al-to-Energy use creates competition to the Al recycling industry, since there is only a limited amount of Al scrap available. It is also important to note that secondary aluminium has a significantly lower environmental impact than primary aluminium, because a large part of the environmental burden is associated with the electric energy use and CO₂ emissions of aluminium smelting (i.e. the process that reduced alumina to aluminium).

The authors point out that the LCA results of this study should not be used for comparative purposes outside of the defined system boundary and the intended application of the system. The system boundaries for both Al-to-Energy conversion sources (primary and secondary) are shown and described in further detail below (Figure 3.9 and Figure 3.10).

The functional unit of both system boundaries is 1 MJ of energy produced from the Al-to-Energy conversion. This amount of energy contains heat and hydrogen. According to the results of the hydrogen production experiments (section 2.2.1), it is assumed that the reaction is complete, i.e. the amount of hydrogen produced is the maximum possible according to the stoichiometric reaction. It is assumed that 90 % of the heat produced can be put to use, corresponding to 45% of the total energy (hydrogen and heat) from the reaction. The required amount of heat for the calcination and casting process and the electricity needed for the smelting process are assumed to be produced by photovoltaic (PV) generated electricity.

This LCA applies an avoided burden approach. Therefore, using aluminium scrap as a resource material for the Al-to-Energy conversion comes with the same initial environmental burdens compared to using primary aluminium. It is important to note that once the end-of-life of the Al-to-Energy conversion is reached, the aluminium leaving the system boundary is assumed to be of high quality and can be used in other products. Therefore, the initial burdens of the resource extraction for the Al-to-Energy conversion will be credited by the avoided burdens of the next product. Comparing both options (primary and scrap Al) using the avoided burden approach, it becomes clear that only aluminium which is lost from the system needs to be replaced and accounted for by new material from bauxite ore (primary aluminium source) or additional aluminium scrap input.

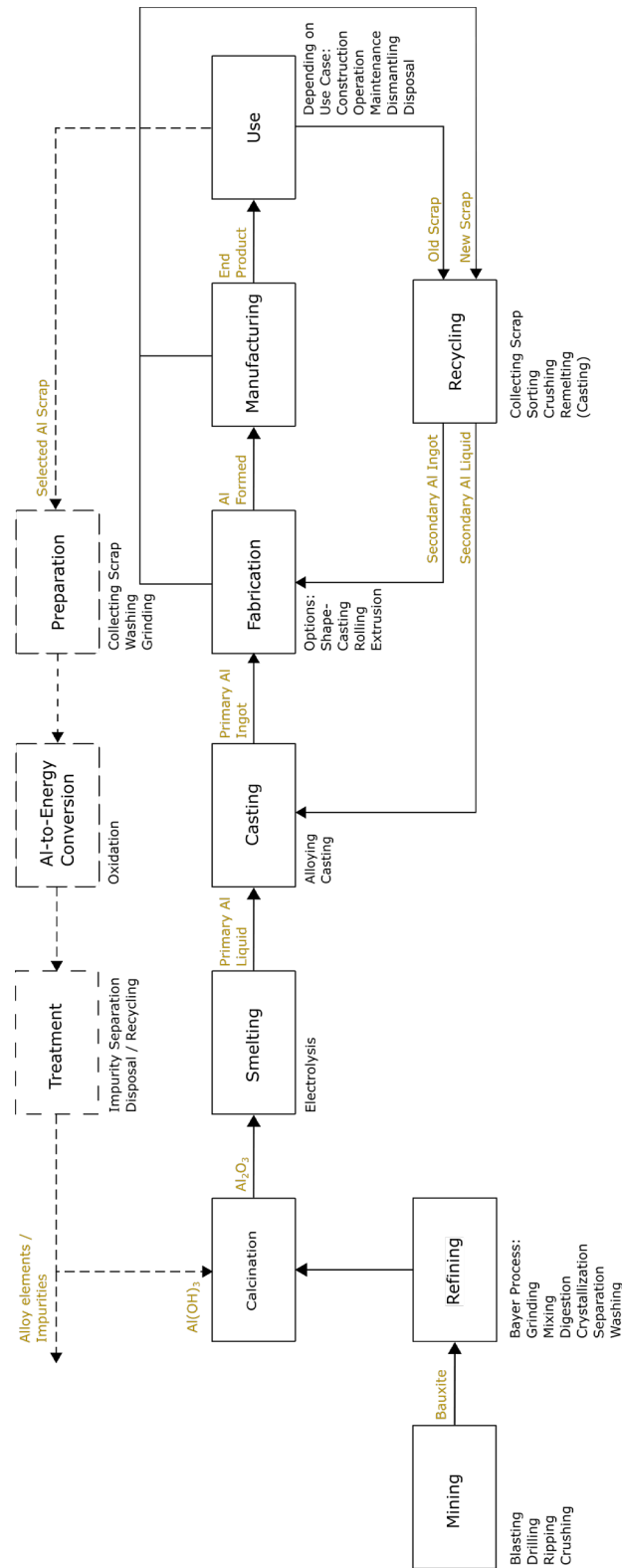


Figure 3.8: General aluminium material flow of the global market. The dotted lines present the additional material flow used for and from the aluminium to energy conversion process, an oxidation process where aluminium reacts with water to aluminium hydroxide (Al(OH)₃). The aluminium hydroxide can be recycled via the calcination process of the Bayer refining method that yield alumina. The alumina is then further smelted to aluminium in order to establish a closed-loop system concept. Aluminium scrap has to be collected, prepared and transported from the industrial site to the end-user, and Al(OH)₃ has to be transported back from the end user to the industrial site.

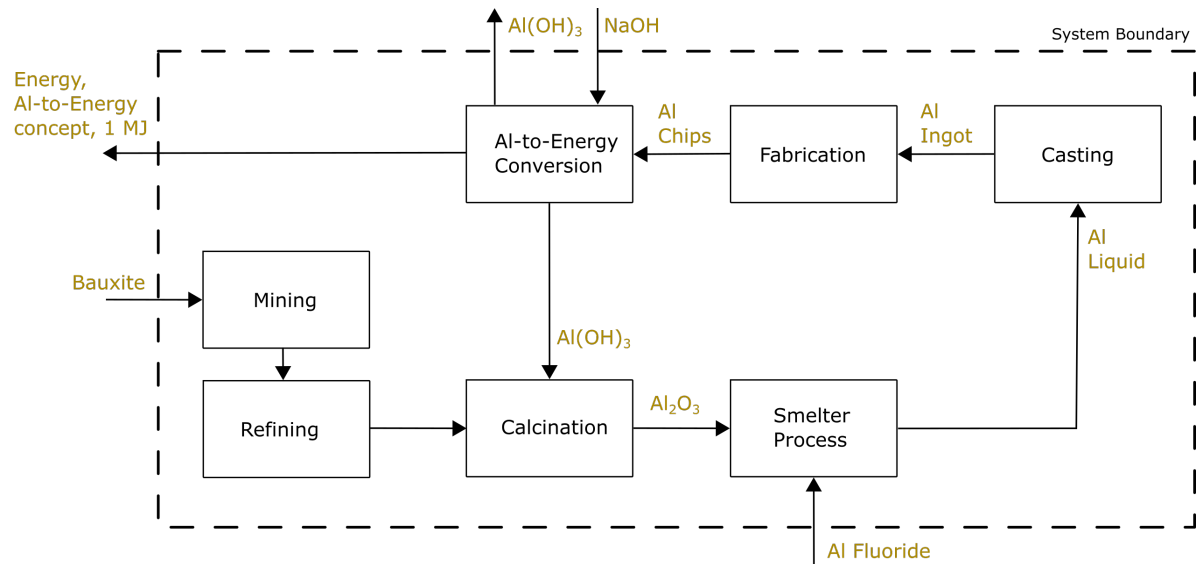


Figure 3.9: LCA system boundary of the Al-to-Energy concept using primary aluminium chips as a source material for the oxidation process. Only aluminium hydroxide ($\text{Al}(\text{OH})_3$) which is lost in the Al-to-Energy conversion process needs to be replaced by the refining of bauxite ore. At the end-of-life, it is assumed that the aluminium ingot is sent to the market.

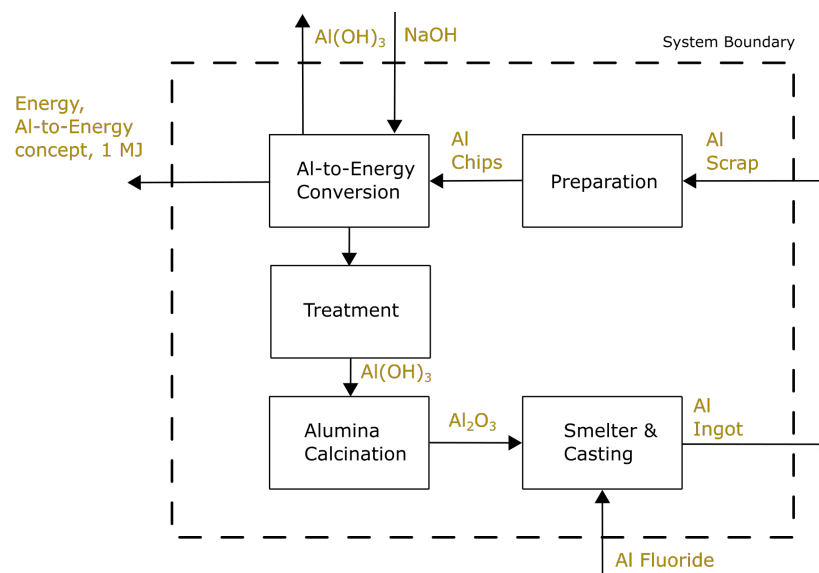


Figure 3.10: LCA system boundary of the Al-to-Energy concept using secondary aluminium chips as a source material for the oxidation process. The produced aluminium ingots are sent to the market and will be used in other products before they are, again, up-cycled in the Al-to-Energy process. The lost aluminium hydroxide in the Al-to-Energy conversion process is offset by a higher input of aluminium scrap.

A detailed description of the processes shown in Figure 3.9 and Figure 3.10 is given in Annex B. When the system boundary of the two material sources, primary Al and secondary Al are compared, it becomes clear that when secondary Al is used, the fabrication process step of the primary Al chips is replaced by the preparation of Al scrap.



In the case of aluminium scrap as a source material of the Al-to-Energy concept, the following preparation steps need to be considered, mainly depending on the material composition:

- Collecting (Transport)
- Shredding
- Washing
- Drying
- De-oiling (Thermal treatment)
- De-lacquering (Thermal treatment)

From chapter 3.1, four categories of Al scrap were identified (Table 3.6). The scrap categories under investigation come from sources with a direct recycling pathway. Therefore, separation from other waste materials were not necessary and was not included in this study.

Table 3.6: Categories of the identified Al scrap material depending on their characteristics.

Al Scrap Source	Description	Al scrap Preparation
Category 1	High Organic Content	Shredding, Washing, Thermal Treatment
Category 2	High Oil Contamination	Shredding, Thermal Treatment
Category 3	High Metallic Impurities	Shredding, Washing, Drying
Category 4	High Aluminium Content	Shredding, Washing, Drying

For all categories, shredding was a necessary process step in order to produce the Al chips. Additionally, thermal treatment was assumed as a process step for scrap material with organic content and oil contamination. Thus, organics and oil can be removed using hot air at a temperature of 500 °C. Washing of the Al scrap was assumed for samples high metallic or organic (in this case ground coffee residues) impurities.

In addition, depending on the quality of the Al chips used, a treatment process of the aluminium hydroxide from the Al-to-Energy conversion is necessary before it can be sent to the calcination process.

3.4.2 LCIA results (GWP) of the aluminium energy storage cycle

In this section, the results of the Life Cycle Impact Assessment (LCIA) are presented for the functional unit of 1 MJ of energy generated (as hydrogen and heat) from seasonally stored renewable energy. In general, only material and energy flows that have a significant influence on the result of the estimated GHG emissions are listed.

Figure 3.11 shows a simplified energy and mass flow Sankey diagram using primary Al as a source material. It is assumed that the Al-to-Energy oxidation reaction takes place in a 6 M sodium hydroxide solution. Material losses in the energy cycle are assumed to be 3 % for



aluminium and 10 % for sodium hydroxide¹. This corresponds to 1.5 g of NaOH per MJ of energy released. Aluminium that is lost is assumed to be replaced by aluminium hydroxide from the Bayer process, i.e. from Bauxite ore.

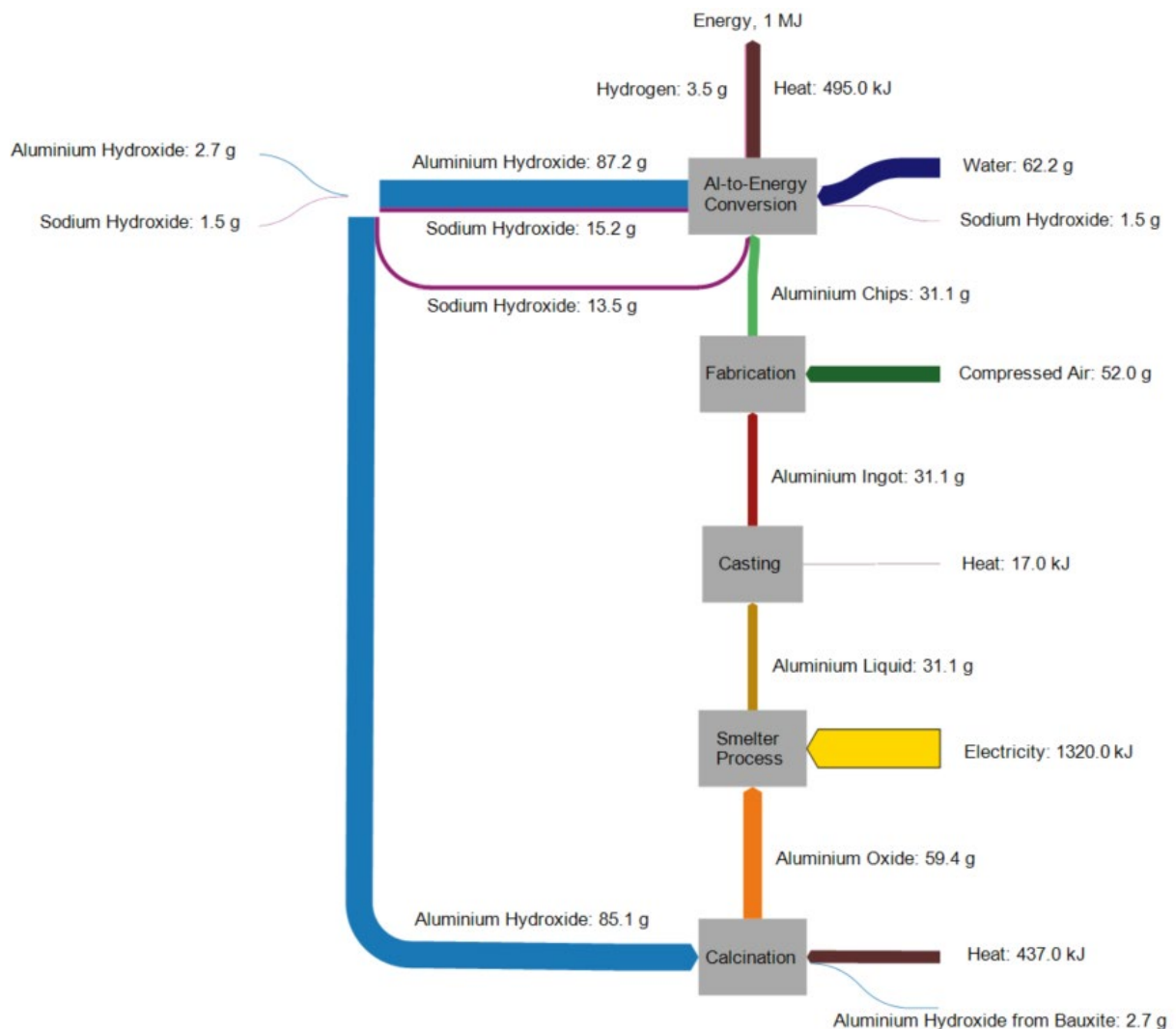


Figure 3.11: Simplified energy and mass flow Sankey diagram of the Al-to-Energy concept using primary Al as a source material, producing 1 MJ of energy. Assumptions for material losses: 10 % for NaOH and 3 % for Al.

The Global Warming Potential (GWP)² is calculated using the IPCC 2013, 100 a LCIA method. Figure 3.12 shows the GWP associated with the different processes and input streams for the concept that uses primary Al as a source.

¹ The 10 % are referring to the amount of NaOH present in a 6 M NaOH solution that contains the stoichiometric amount of water needed for the reaction. As NaOH is not consumed by the reaction, no NaOH would have to be replaced in the ideal "loss-free" case. However, XRF of aluminium hydroxide produced in this project indicates that about 6-10 % of the NaOH ends up in the aluminium hydroxide sample even if this is rinsed to neutral pH after removal from the reaction vessel.

² The GWP is a measure of the emissions of greenhouse gases (GHG) such as CO₂, perfluorocarbon (PFC), and methane (CH₄), and is expressed as kilogram of CO₂ equivalent (CO₂eq).

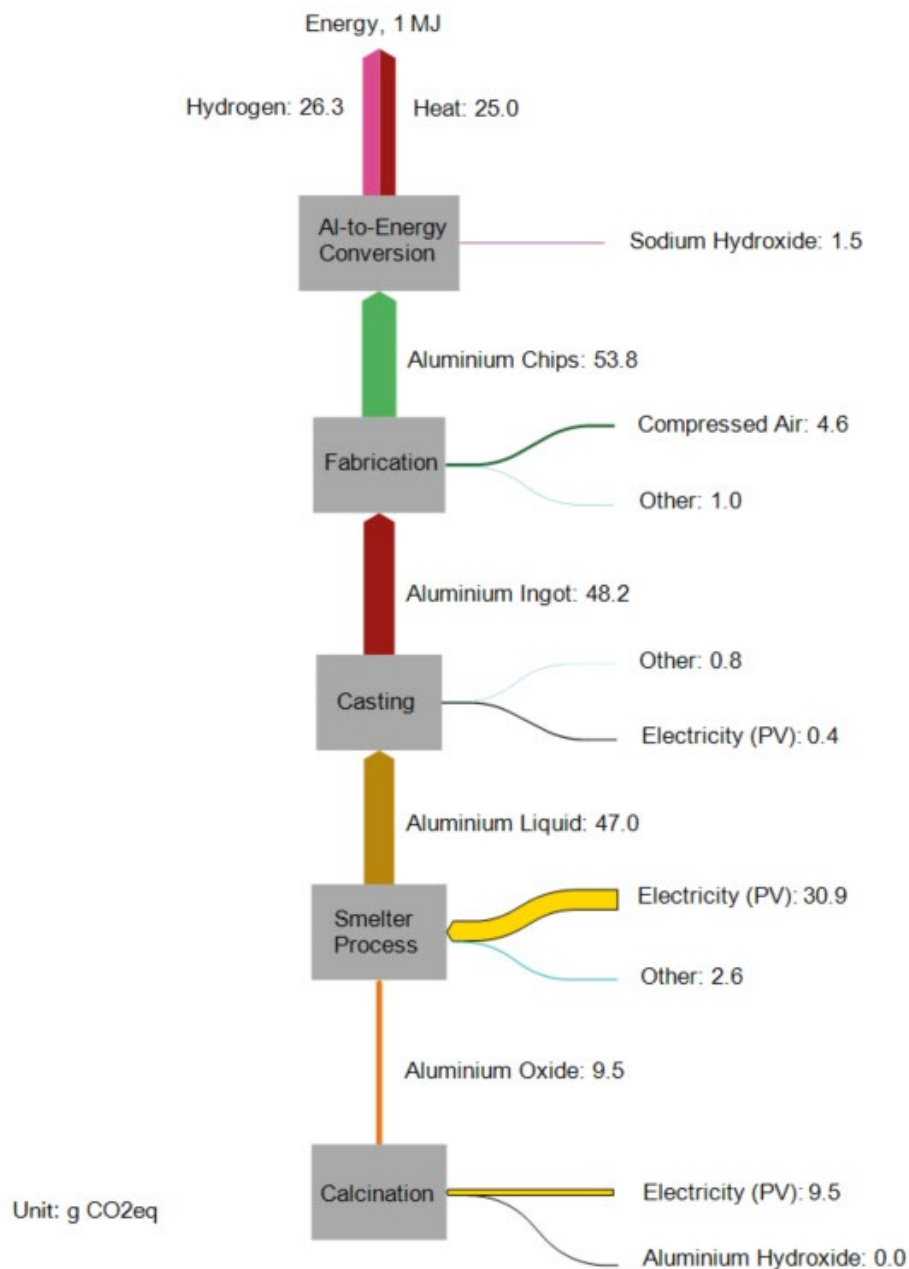


Figure 3.12: Global Warming Potential (GWP) in g CO₂eq/MJ for the Al-to-Energy concept using primary Al as the source material. The allocation of the GHG emissions to the heat and hydrogen production was based on its energy content. Data from Ecoinvent version 3.1 (GWP of electricity from PV 21 g CO₂eq/MJ_e).

The estimated total GHG emissions related to the production of 1 MJ of energy with this concept is 51.3 g CO₂eq.

Figure 3.13 presents the attribution of GHG emissions to the different system processes. It can be seen that about 60 % of the GHG emissions can be allocated to the smelting process using inert anodes. This is mainly due to the GWP that is related to the electricity generated by PV, in combination with the significant amount of this electricity needed in the electro-winning process that generates aluminium from alumina. The second highest share (about 17 %) of



the estimated GHG emissions can be attributed to the PV electricity used for the calcination process. This process is still thermodynamically inefficient today. Third main contributor is the fabrication of chips or granules from the ingot with about 10 %. The casting process represents only about 3 % and the Al-to-Energy conversion process 0.2 to 3 % of the estimated overall GHG emissions (depending on the sodium hydroxide loss rate). The GWP of the estimated Al(OH)_3 loss rate (3 %) and the transportation of the source and product material (approx. 175 km by train and 170 km by lorry per direction, extracted from Ecoinvent reference dataset heating oil) are negligible.

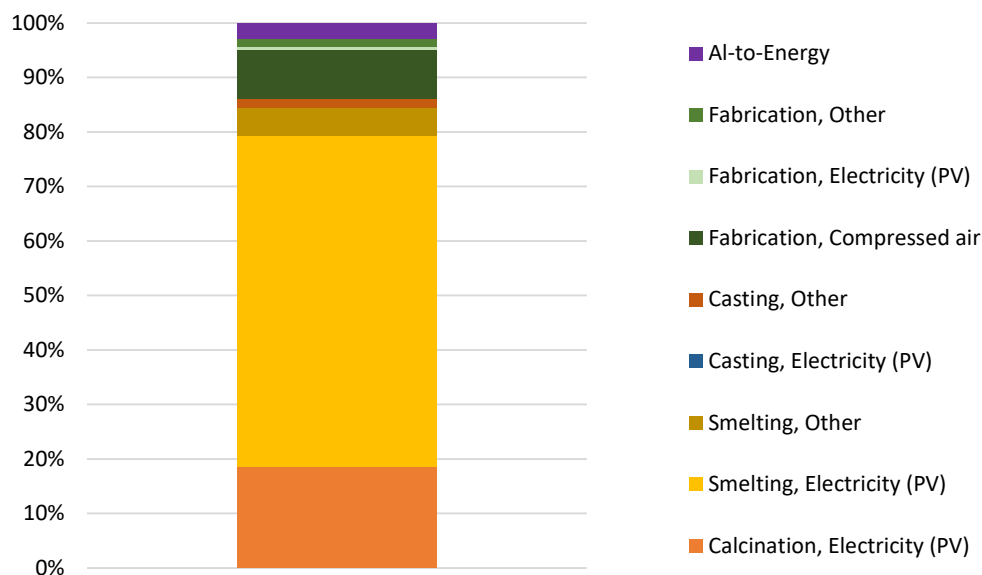


Figure 3.13: Share of GHG emissions related to the different processes and inputs, using primary Al as a source material (loss of NaOH: 10 % included in the Al-to-Energy process, loss of Al: 3 % as Al(OH)_3).

It is important to point out that the results are based on the background Ecoinvent dataset version 3.1 "Electricity, production mix photovoltaic, at plant/CH" which corresponds to 21 $\text{gCO}_2\text{eq/MJ}_e$. However, Frischknecht et al. [9] recently published new datasets for the electricity production from PV, where the average Swiss PV module supplier mix from 2019 reach GHG emissions of approx. 8.9 $\text{gCO}_2\text{eq/MJ}_e$ (with a yield of 975 kWh/kW_p). Furthermore, Müller et al. from Fraunhofer ISE conducted a similar study [10] with similar results. They conclude that one of the main reasons for the overestimation of the GWP in the Ecoinvent dataset is caused by outdated electricity mix datasets used in the production of the PV modules. Based on their own methodology and depending on the PV technology, GHG emissions for electricity from PV is estimated to reach 4.89 and 3.58 $\text{gCO}_2\text{eq/MJ}_e$ when PV modules are produced in the EU, 5.94 and 4.47 $\text{gCO}_2\text{eq/MJ}_e$, when produced in Germany, and 8.31 and 6.44 $\text{gCO}_2\text{eq/MJ}_e$ when produced in China. These results are based on an average European installation location (solar irradiation 1391 $\text{kWh}/(\text{m}^2\text{yr})$).

As the GWP of the Al-to-Energy concept is dominated by the emissions of the electricity production that drives both, the smelter process as well as the calcination, the assumptions for



the source of the electricity influence the results significantly. Thus, the estimated total GWP declines from about 50 g CO₂eq/MJ for PV electricity production using the dataset of Ecoinvent to less than 30 g CO₂eq/MJ when more recent and more favourable data for the production of PV modules are assumed (Figure 3.14), which leads to a reduction of 46 %. Compared to this significant influence, the influence of the sodium hydroxide loss rate is minor (1 – 2 %).

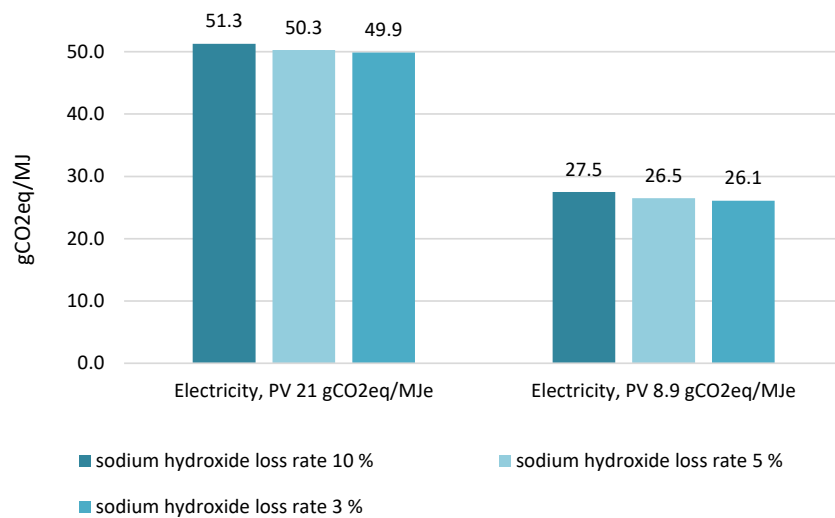


Figure 3.14: Estimated total GHG emission per 1 MJ of energy produced using primary Al as the source material with available background datasets for electricity generation from PV and various loss-rates for sodium hydroxide.

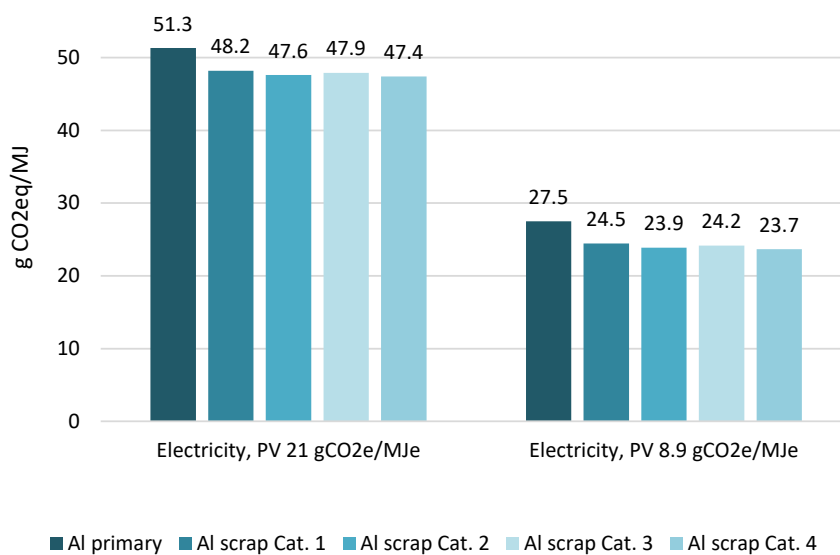


Figure 3.15: Total estimated GHG emission per 1 MJ of energy produced using Al scrap as the source material compared to primary Al. The results of GHG emissions are based on the various Al scrap and a sodium hydroxide loss rate of 10 %.



GHG emission can be reduced by 5 to 6 % if Al scrap is used as a source material when compared to the scenario with primary Al as a source material. The results of the estimated GHG emissions from the various Al scrap materials differ from 1.1 to 1.5 % (Figure 3.15) depending on the necessary cleaning and preparation process.

One of the reasons for the rather small difference in GWP (approx. 3 g CO₂eq/MJ) between using primary or scrap aluminium is the choice of the allocation method, as described in Annex A and the closed-loop concept of both scenarios. Since this LCA applies the avoided burden approach, the initial environmental impact of the source material (primary and Al scrap) is the same. This is because of the recycling concept and the resulting credit by the avoided burdens of the next product. Only the last product disposing the material does not receive this credit. Therefore, it is important to point out that this LCA assumed a recycling of aluminium hydroxide or up-cycling to primary aluminium at the end-of-life (EOL) and reuse in other products. Another reason is the very low amount of GHG emissions attributed to aluminium hydroxide. This is because the majority of the environmental impact of the Bayer process stems from the energy use for calcination (production of aluminium oxide from aluminium hydroxide), which is part of both system concepts and therefore part of the material and energy cycle.

However, the scenario using scrap material reached lower estimated GHG emissions primarily because the environmental impact allocated to the production of aluminium chips from Al scrap is less energy and material intensive than the production of chips from an ingot. This is because the investigated scrap materials were already broken down into small or thin pieces can be easily crushed to aluminium chips. Thus, no milling or cooling is needed. Based on Ecoinvent reference data, it can be assumed that the milling of aluminium ingots results in higher GHG emissions when compared to the cleaning and thermal treatment of the scrap metal.

Figure 3.16 shows the GHG emissions of the different processes using Al scrap category 1 as a source material, with a loss rate of 10 % for sodium hydroxide and 3 % for Al. In this case, the produced aluminium ingot leaves the system boundary of the Al-to-Energy concept to product B. However, after its lifetime, product B makes this used aluminium available for recycling as post-consumer Al scrap or old Al scrap which re-enters the system boundary of the Al-to-Energy concept into the preparation process.

It is important to note that any additional environmental effects from efforts for producing product B from the ingot need to be allocated to product B, and thus are not attributed to the Al-to-Energy system. The difference of 1.6 g CO₂eq/MJ between the material leaving the casting process for product B and the material returning from product B entering the preparation process is a result of the collection and transportation efforts for the Al scrap material, based on the Ecoinvent reference dataset

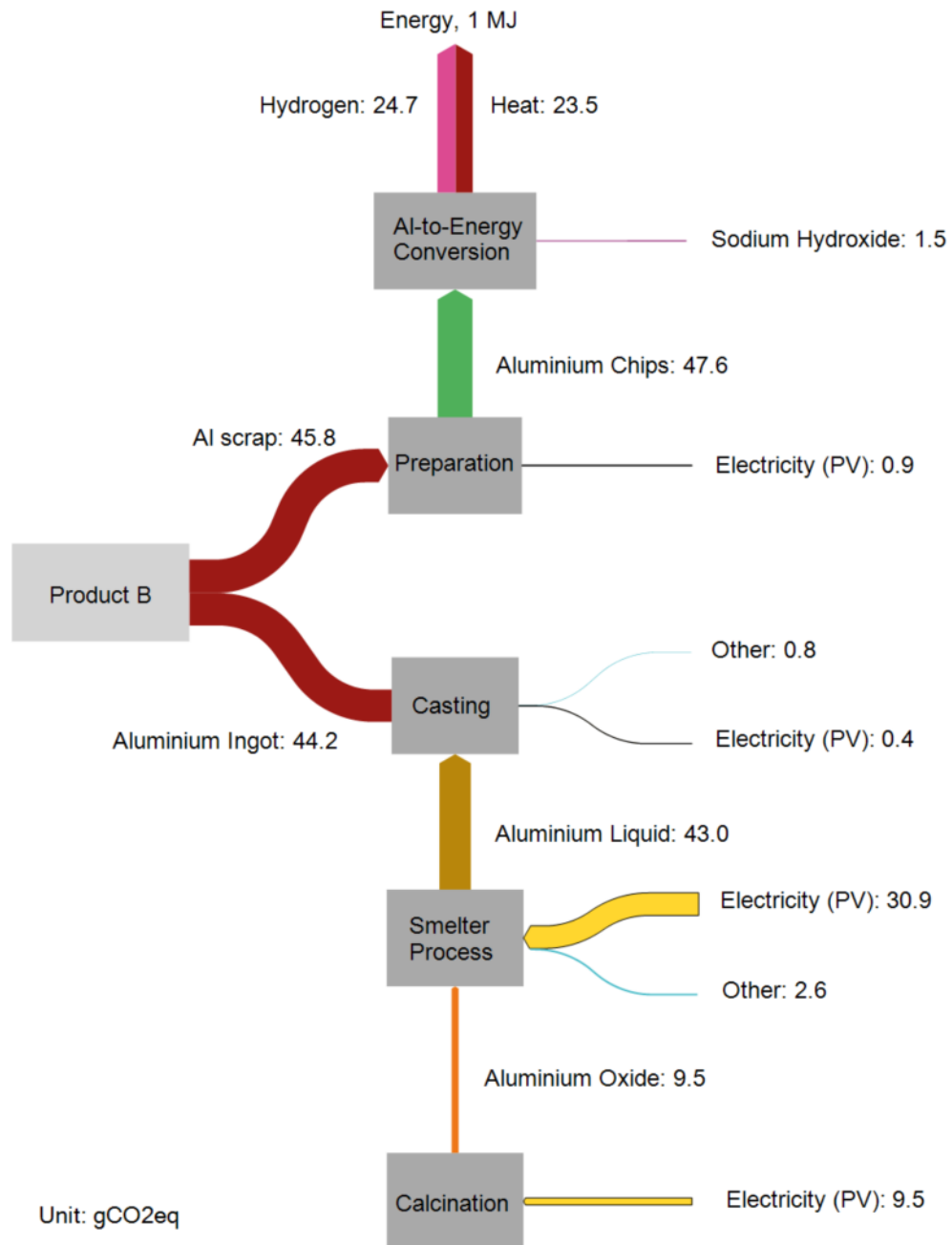


Figure 3.16: Global Warming Potential (GWP) in gCO₂eq/MJ for the Al-to-Energy concept using Al scrap category 1. The allocation of the GHG emissions to the heat and hydrogen production is based on its energy content. The results refer to a loss rate of 10 % for sodium hydroxide and 3 % for Al with a GWP for the electricity from PV of 21 gCO₂eq/MJ_e.



3.4.3 Comparison of the Al-to-Energy system to a Mini-CHP plant using natural gas

In this section the GWP of the Al-to-Energy process is compared with an alternative technology that can provide electricity and heat in winter, and which is suitable for the installation in residential buildings for covering space heating and electric energy demand. For this purpose, a Polymer Electrolyte Membrane (PEM) fuel cell system was added to the Al-to-Energy system in order to convert the produced hydrogen to electricity and heat, and a natural gas CHP unit has been chosen for comparison.

Thus, the new functional unit used in this section represents 1 MJ of energy as the total of heat and electricity. For the conversion of hydrogen, it was assumed that the electric efficiency of the hydrogen fuel cell is 50 % (HHV), and that 45% of HHV can be made available as useful heat.

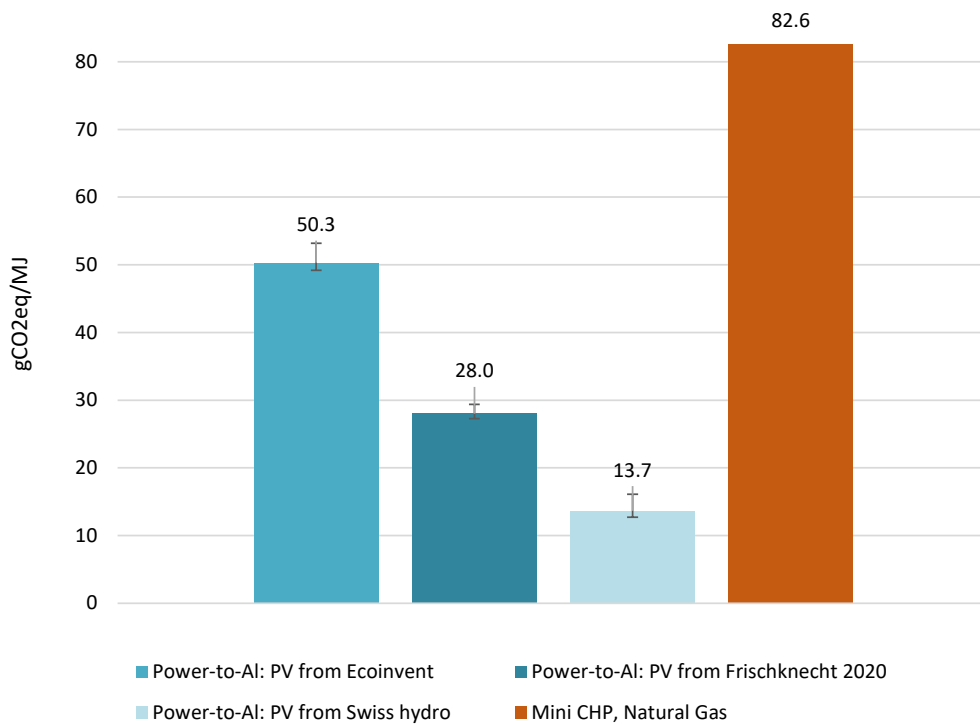


Figure 3.17: Average total life cycle GHG emission of the Al-to-Energy concept per 1 MJ of energy produced using primary and scrap Al as the source material (min. and max. values are indicated by the error bar). The Al-to-Energy results are based on PV from Ecoinvent "photovoltaic, at plant/CH" (21 gCO₂eq/MJ_e), values by Frischknecht et al. 2020 [9] (8.9 gCO₂eq/MJ_e) as well the Swiss mix of electricity production from hydropower (1.3 gCO₂eq/MJ_e). Size of mini-CHP plant: 2 kW_e.

Figure 3.17 presents the estimated life cycle GHG emissions from the Al-to-Energy concept, using primary and scrap Al as a source material including a PEM fuel cell system. In this case, the functional unit of the Al-to-Energy concept represents 1 MJ of energy containing 0.748 MJ of heat and 0.253 MJ of electricity. The Al-to-Energy system is compared to a mini CHP system (2kW_e) using natural gas as the fuel based on the available Ecoinvent dataset. It is important to note that the share of heat and electricity of the functional unit slightly differs, depending on the CHP technology. Therefore, the functional unit of the mini-CHP system was assumed to be 1 MJ of energy containing 0.723 MJ of heat and 0.277 MJ of electricity. This dataset estimates a fuel to electric efficiency of 25 % (HHV) with a total efficiency of 85 %.



Depending on the background dataset used for the PV electricity production, the Al-to-Energy system can reduce GHG emissions from 33 to 64 % per MJ of energy produced when compared to an alternative mini CHP plant. If a mix of electricity from hydropower (46 % Run-of-River and 53 % from storage hydropower) would be used for the calcination and smelter process instead of PV electricity, a GHG emission reduction of over 80 % could be achieved. As soon as the GWP of the electricity mix that is used for the production of aluminium from aluminium hydroxide – including calcination - exceeds 39 gCO₂/MJ_e, a CHP unit based on aluminium is no longer reducing greenhouse gas emissions compared to a CHP unit that is based on natural gas.

3.5 Cost and use of reaction products

3.5.1 Cost scenarios

The following section provides an overview of potential costs, cost savings and other market opportunities for the recycling of aluminium hydroxide or alumina produced from the Al-to-Energy system. For the cost estimations, metric tonne (mt) was used for the definition of the mass unit.

In general, cost advantages for using Al scrap instead of primary Al for the Al-to-Energy processes will stem from the fact that recycling materials are cheaper than primary Al. The cost of primary aluminium on the world market ranged from 1500 to over 3000 USD/mt (Figure 3.18) within 2016 and 2021³.



Figure 3.18: Price evolution of aluminium in USD/mt from 2016 to 2021⁴.

³ Before the Covid pandemic, Al-prices were around 2000 USD/mt. During the pandemic, the price has risen to over 3000 USD and dropped to 2700 USD again.

⁴ <https://tradingeconomics.com/commodity/aluminum>.



The London metal exchange (LME) also lists different aluminium products, including scrap from used beverage cans (UBCS) and alumina (Table 3.7).

Table 3.7: London Metal Exchange (LME) prices for different aluminium products and for alumina (25.11.2021).

	USD	€
Al (cash offer)	2699	2402
Al Alloy (cash offer)	2406	2141
Al Scrap UBCS US (Argus) - 3 months closing	2020	1798
Alumina (Platts)	408	363

Prices are given in USD and converted with the exchange rate of Nov. 25, 2021: 0.89 €/USD.

Table 3.8 lists prices given by various partners of the AlEnCycles project for different Al recycling materials. It can be seen that the prices for Al recycling materials varies significantly from 315 € (coffee capsules) to 2020 € (UBCS traded at the LME).

Table 3.8: Prices given by various partners of the AlEnCycles project for different Al-waste / recycling materials.

	CHF/mt	€/mt
Al capsules (S1-S4)	330	315
Al used beverage cans (S5)		1500
Al chips, wet (S6)		1450
Al chips, dry (S7)		1650

Prices given in CHF were converted to € with the exchange rate of Nov. 25, 2021: 0.95 €/CHF.

Two different cases have to be distinguished for the use of recycling / scrap material for Al-to-Energy processes:

- A. **Closed loop:** Al recycling material is introduced into the Al energy cycle at the beginning, and produced aluminium hydroxide is being used for the production of new aluminium. In this case, the Al material flow stays within the Al-to-Energy cycle after the first introduction. Thus, cost savings are only effective in the first year of introduction, since no (loss free cycle) or only little amounts of Al (to compensate material losses within the cycle) are introduced every year.
- B. **Open system:** Al recycling material is being used for the Al-to-Energy production and the resulting aluminium hydroxide is sold to be re-used in other processes, e.g. as a flame retardant additive. Thus, all Al used for the Al-to-Energy cycle is introduced from scrap every year.

Obviously, only minor cost reduction can be achieved for case A), where cost savings occur only in the first year, whereas much higher cost savings may be achieved in case B), where scrap material is being used for the Al-to-Energy process every year. However, case A is dependent on the question whether the produced aluminium hydroxide is suitable for the



aluminium electrolysis process, and part B is dependent on the question whether there will be any market and demand for the resulting aluminium hydroxide.

The amount of Al material that needs to be purchased and $\text{Al}(\text{OH})_3$ that can be sold over a lifetime of 25 years is shown in Table 3.9, for primary and closed cycles as well as for the open cycle variant. Assumptions for cost of primary Al and high quality (smelter grade) $\text{Al}(\text{OH})_3$ are based on the past five years of market history (2000 and 187 €/mt respectively). For scrap Al a relatively low price of 350 €/mt is assumed. For low quality $\text{Al}(\text{OH})_3$, that contains many metal impurities, it is expected that it can be added into the Bayer process instead of Bauxite ore and thus the market price is assumed to be 45 €/mt, i.e. similar as the present market price for Bauxite ore.

The results of Table 3.9 indicate that the net (Al) material cost leads to a cost per kWh of energy from Al in the range of -20 to 130 €/MWh. The column on the rightmost side shows a hypothetical case for an open cycle concept where high quality $\text{Al}(\text{OH})_3$ could be produced from low value scrap, i.e. the recycling material would be "cleaned" during the process. In this case, the net material cost, i.e. cost of purchase minus revenue from the sales of $\text{Al}(\text{OH})_3$, could even be negative and thus an economic benefit would result from the purchase and sales of the Al containing materials. However, this cost does not yet include any additional process steps for purification of material and thus does not give a complete picture of the full cost. Furthermore, for the closed cycle cases, cost of aluminium smelting would have to be added, which is further outlined in the next section.

Table 3.9: Amount of material and net cost of Al purchase and $\text{Al}(\text{OH})_3$ sales for 25 years, absolute and per MWh of energy delivered from stored energy in Al, assuming 3% Al losses per year, cost of primary Al: 2000 €/mt, scrap Al: 350 €/mt, high quality $\text{Al}(\text{OH})_3$: 187 €/mt, low quality $\text{Al}(\text{OH})_3$: 45 €/mt .

Amounts (mt)	Primary Al.	high value scrap; high quality $\text{Al}(\text{OH})_3$		low value scrap; low quality $\text{Al}(\text{OH})_3$		low value scrap; high value $\text{Al}(\text{OH})_3$	
		closed cycle	open cycle	closed cycle	open cycle	closed cycle	open cycle
Al material inputs	1.75	1.75	25.00	1.75	25.00	1.75	25.00
Al-hydroxide sales	2.80	2.80	70.08	2.80	70.08	2.80	70.08
Cost (€)							
Aluminium material input	3500	2888	41250	613	8750	613	8750
Sales of Al-hydroxide	-524	-524	-13105	-126	-3154	-524	-13105
Total cost of raw material	2976	2363	28145	486	5596	88	-4355
annual cost of raw material	119	95	1126	19	224	4	-174
cost per MWh	14	11	129	2	26	0.4	-20



Von Kaenel and De Nora [11] estimated operating cost for an inert electrode aluminium smelter, excluding energy and alumina purchase, to be about 130 €/mt of produced Al. Not included were capital cost of the plant, that can be assumed as 230 €/mt⁵. For a plant that is only operated 1/3 of the year (2920 hours), we assume that the operating cost per mt is constant, but the capital cost is 3*230 €/mt, which leads to a total cost of 820 €/t of Al or 9.4 €-cents/kWh stored energy from Power-to-Al.⁶ This cost is significantly lower than cost for seasonal storage by Power-to-Methane, where methane has to be compressed or liquefied and stored in pressurized tanks or cryogenic tanks.

3.5.2 Use of aluminium hydroxide from the reactions

In order to estimate the market value of aluminium hydroxide from Al-to-Energy reactions, samples were sent to TRIMET Aluminium SE in Germany and analysed by Terrachem GmbH. Table 3.10 shows the results of the analysis after calcination, assuming that all metals detected where in the form of oxides. The rightmost column contains the requirements for smelter grade alumina that is used by TRIMET. It can be seen that none of the aluminium hydroxide samples fulfils this requirement. However, it also has to be considered that the uncertainty of the XRF analysis may in some cases (e.g. S8) be higher than the difference between the obtained result and the requirements for smelter grade alumina.

Table 3.10: Concentration (wt.%) of the different components after calcination for 1h at 1050°C, with light grey values that are not in the range required for a conventional aluminium electrolysis process.

	S0	S1	S2	S3	S4	S5	S6	S7	S8	Req.
Al ₂ O ₃	97.79	95.08	96.96	97.03	96.99	93.57	92.76	97.45	98.12	98.6
Na ₂ O	1.93	1.36	1.20	1.53	1.55	1.57	1.72	1.54	1.64	0.4
MgO		1.15				2.34	2.30	0.40		
Fe ₂ O ₃	0.17	0.97	1.49	1.30	1.33	0.76	0.69	0.27	0.14	0.015
MnO		0.72	0.05	0.02	0.02	0.79	0.38	0.05		0.002
SiO ₂	0.06	0.48	0.11	0.08	0.06	0.47	1.28	0.14	0.05	0.03
CaO	0.03					0.15	0.03	0.03		0.04
ZnO	0.01	0.06	0.02	0.02	0.02	0.08	0.52	0.03		0.010
CuO		0.11	0.09	0.02	0.02	0.11	0.14	0.08	0.05	
TiO ₂		0.05	0.08			0.09				0.005
Cr ₂ O ₃		0.02				0.03	0.14			
NiO		0.02	0.02	0.02	0.02	0.03	0.05	0.02	0.02	

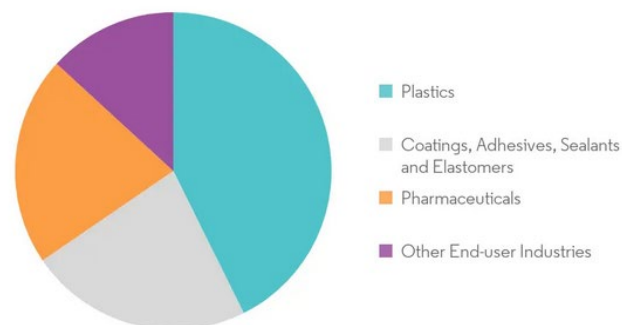
⁵ Personal communication by an aluminium industry expert, source not disclosed.

⁶ Not included in this cost are electricity price, transport of material and the conversion of Al back to energy in decentralized units (Al-to-Energy).



However, for most samples, especially for the ones from recycling material, additional treatment and purification steps would be needed in order to use them in a conventional aluminium smelter, and it can be assumed that the market value of the produced aluminium hydroxide is therefore rather low.

As can be seen from Figure 3.19, the global market of aluminium hydroxide is dominated by plastics industry, coatings adhesives, sealants and elastomers, and pharmaceuticals. However, all applications that were included in this report are requiring an aluminium hydroxide with higher quality than resulting from Al-to-Energy processes when scrap aluminium is used and no additional purification steps are applied.



Source : Mordor Intelligence



Figure 3.19: Global market share of aluminium hydroxide by End-user Industry in 2019.

Another possibility would be to find use for alumina after calcination of the aluminium hydroxide. As shown in Figure 3.20, this market is highly dominated by the use for the production of aluminium. Ultra-pure, white aluminium oxide is also used in the cosmetics industry, especially as microdermabrasion crystals for exfoliation creams and skin treatments as a 99.4 wt.-% (with 0.43 wt.-% Na_2O , and 0.03 wt.-% Fe_2O_3) abrasive media. Nanoparticles of aluminium oxide are versatile absorbents used for purification of water / waste water applications [12]. Also activated alumina in spherical shape (≥ 93 wt.-% $\gamma\text{-Al}_2\text{O}_3$ with ≤ 0.3 wt.-% Na_2O) are used as a filter of fluoride, arsenic and selenium in drinking water [13]. There are also other catalytical applications used for drying processes, etc. with such spherical products. Furthermore, inert ceramic balls with a high SiO_2 content (70 to 77 wt.-%) and approx. 18 wt.-% Al_2O_3 with up to 2 wt.-% of Na_2O are typically used as a catalyst bed support or as a protection material in the refractory industry [14]. In the ceramic industry, Al_2O_3 material with 92 and 95 wt.-% content (max. 0.1 wt.-% Na_2O) and sintering temperatures of 1580 or 1620 °C are available on the market [15]. Finally, also in this case it seems not easy to find a direct application of the alumina produced from Al-to-Energy based on recycling materials, unless further purification steps are included in the process.

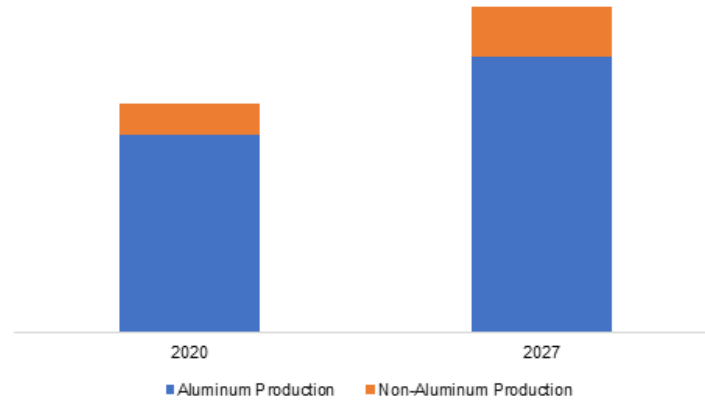


Figure 3.20: Global share of alumina application in 2020 and 2027.



4 Conclusions

4.1 Aluminium materials and conversion to heat and hydrogen

All scrap Al materials reacted with water under the tested conditions and produced hydrogen and heat. With the exception of one sample, reaction was complete and the amount of hydrogen that could be expected from the stoichiometric reaction of Al and other hydrogen forming metals in the samples was obtained (within the limits of measurement uncertainty). Only sample 5 (aluminium pop cans) reached with 89% a bit less conversion efficiency than the others did. The cost of the scrap materials shows a high variability from roughly 300 €/mt to almost the price of primary aluminium (1'800 €/mt).

Scrap materials showed various organic impurities (coffee residues, plastics, oil) that were removed by shredding and washing. A further reduction of organic materials could be achieved by thermal treatment. This reduced sample weight, depending on the origin of the sample from 0 – 37%. Analysis of elemental composition (ICP-OES) after thermal treatment showed metallic impurities mainly of Fe (almost all samples), Mg (three samples) and for two samples additionally other elements.

Resulting solid products from the conversion to heat and hydrogen contained mainly $\text{Al}(\text{OH})_3$. No significant differences could be detected by XRD. However, analysed by XRF revealed other elements that are unwanted in the electrolysis process. The amount of sodium that ends up in the solid reaction products mix that is removed from the system can be influenced substantially by post-treatment (rinsing/washing). However, even after treatment it still leads to a considerable loss of $\text{Al}(\text{OH})_3$ from the reaction system. It can be assumed that most metals that can be found in the aluminium hydroxide will still be present as oxides after calcination. Sodium does not represent a major problem, as it is present in the electrolyte anyway and can be compensated by adding complementary electrolyte components. However, some of the detected elements like iron, copper, zinc and manganese are problematic as aluminium produced would contain too high shares of these elements and could not be sold as a high quality primary aluminium on the market.

For this reason, either purification steps would have to be introduced before or after the Al-to-Energy reaction, or a different market would have to be found for the resulting aluminium hydroxide or aluminium oxide after calcination. At present, a market that would demand low quality aluminium hydroxide could not be identified. This leaves the option of either testing different ways for purification, e.g. via the Bayer process, or targeting new small-scale inert smelters that would produce a different (low quality) aluminium just for energetic use.

4.2 GWP based on Life Cycle Assessment

Based on the LCA that used the avoided burden approach, it could be established that the selection of the source material only had a minor influence (1 to 2 %) on the estimated total GHG emissions of the Al-to-Energy system. The same can be concluded for the sodium hydroxide loss rate that was varied from 3 to 10% (estimation according to measurements in this project was 6-10%). However, the selection of the electricity that is used for the (inert electrode) smelter process as well as for the production of heat for calcination had a significant



influence (more than 80 % of GWP). Based on literature, it was found that the current datasets of Ecoinvent on electricity production by PV are outdated and needed to be investigated in further detail. The results presented in this study show the GWP (IPCC 2013 100-year method) using the Ecoinvent dataset from 2005 for the electricity production from PV and an updated dataset (2020) by Frischknecht et al. [9]. Müller et al. [10] argues that the reason for overestimation of the GWP burden of PV electricity is the usage of outdated background datasets for the electricity mix used for the PV module production.

In order to compare the GWP of heat and electricity from the Al-to-Energy system with an alternative mini CHP plant, a PEM fuel cell system was added to the system boundary of Al-to-Energy. Depending on the electric energy source used for calcination and smelting, the GWP for heat and hydrogen from Al-to-Energy is

- 50 gCO₂eq/MJ for PV electricity from "old" Ecoinvent dataset
- 28 gCO₂eq/MJ for newer datasets provided by Frischknecht
- 14 gCO₂eq/MJ for a mix of Swiss hydro-power

Heat and electricity from a natural gas micro-CHP unit (2 kW_e) has a GWP of 83 gCO₂eq/MJ, which is 60 – 500% more than can be expected from Al-to-Energy systems that use aluminium produced with renewables in inert anode smelter processes.

Thus, regarding the life cycle GHG emissions of the Al-to-Energy conversion it can be concluded that the proposed concept can achieve much better performance when compared to alternative mini CHP plants using natural gas as a fuel. However, further impact categories should be considered in order to investigate not only the GWP but also freshwater ecotoxicity, water resource depletion, etc. Unfortunately, this could not be further examined due to the project time frame and resources but will be the topic of further investigations.

5 National and international cooperation

Within Switzerland, we cooperated with Nestlé Nespresso that supplied the coffee capsule waste for use in Al-to-Energy conversion, as well as with Solenthaler Recycling AG and Aluminium Laufen AG for the supply of other aluminium materials. Analysis of suitability of reaction products was done with the help of TRIMET Aluminium SE in Germany. Energie 360° AG and EWJR provided important insights into energy services, transport logistics, safety of transport, and cost of transport both for solid fuels and for electricity.



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Annex A: Life cycle inventory (LCI)

In order to establish the LCI data collection for the aluminium material flow of the charging process (calcination, smelter process and casting), two LCA studies published by the International Aluminium Institute (IAI) and the European Aluminium Association (EAA) [16], [17] serve as a basis to allocate the most important background LCI by life cycle stages and select the correct existing Ecoinvent datasets. The level of detail of the LCI and minor or negligible inputs and outputs that will not significantly change the overall conclusions of the study are determined and subsequently omitted.

The following cut-off rules (Figure 6.1) were applied where necessary.

Table 6.1: Summary of the cut-off rules.

Included	Excluded
• Raw material extraction • Energy and fuel inputs • Extraction, processing and delivery of energy and the fuel inputs • Extraction and processing of auxiliary materials (e.g. chemicals, solvents, lubricants, packaging, etc.) • Production of the source material and processing it • Transportation of raw and processed materials and products • Source material recycling • Waste treatment and disposal • Main production facilities construction	• Construction material for Al-to-Energy converter • Capital equipment and maintenance • Maintenance and operation of equipment • Human labour • Anode production for inert smelter process • Voltage transmission losses from PV • Process heat losses and thermal storage • Heat exchanger losses and heat distribution • Battery storage for generated electricity

Regarding the allocation method that can be used to determine the impact of recycling metals, the ISO 14044 [7] supports a) an allocation between the primary production and the recycled products, cut-off or recycled content approach (Section 4.3.4.3.4 of ISO 14044) and b) an open-loop scenario with a closed loop recycling procedure, end-of-life recycling or avoided burden approach (Section 4.3.4.3.3 of ISO 14044). In general, the recycled content [18] approach assumes benefits to increased recycled content at the time of production. Its aim is to promote a market for recycled materials that is otherwise limited, uneconomic, or immature. The end-of-life (EOL) recycling approach indicates increased impacts at the time of production, offset by negative impacts in future years, therefore, this concept is based on the premise that materials not recycled need to be replaced by primary materials.

The selection of the LCA approach, in this case, has a major influence on the environmental results of recycled metal. Dubreuil et al. [18] points out, that the metal industry strongly



supports the end-of-life recycling (avoided burden) approach over the recycled content approach (cut-off method) for the purposes of environmental modelling, decision-making, and policy discussions involving recycling of metals. In this regard, Frischknecht [19] concludes, that the correct or appropriate approach of recycling processes cannot be solved by science only and clear statements from commissioners of LCA about the sustainability concept and risk perceptions are necessary.

Figure 6.1 shows both approaches applied to the Al-to-Energy process. If this LCA would not consider a circular economy concept, meaning the recycling of aluminium hydroxide to the aluminium source material, the recycling content approach could be applied. However, both system boundaries shown in Figure 3.9 and Figure 3.10 include the recycling and the replacement of the primary source material. Therefore, this LCA applies the avoided burden approach. Nevertheless, the avoided burden approach does require that the primary burdens of a recycled material used in a product is not cut-off. Therefore, using aluminium scrap as a resource material for the Al-to-Energy conversion comes with the same initial environmental burdens compared to using primary aluminium.

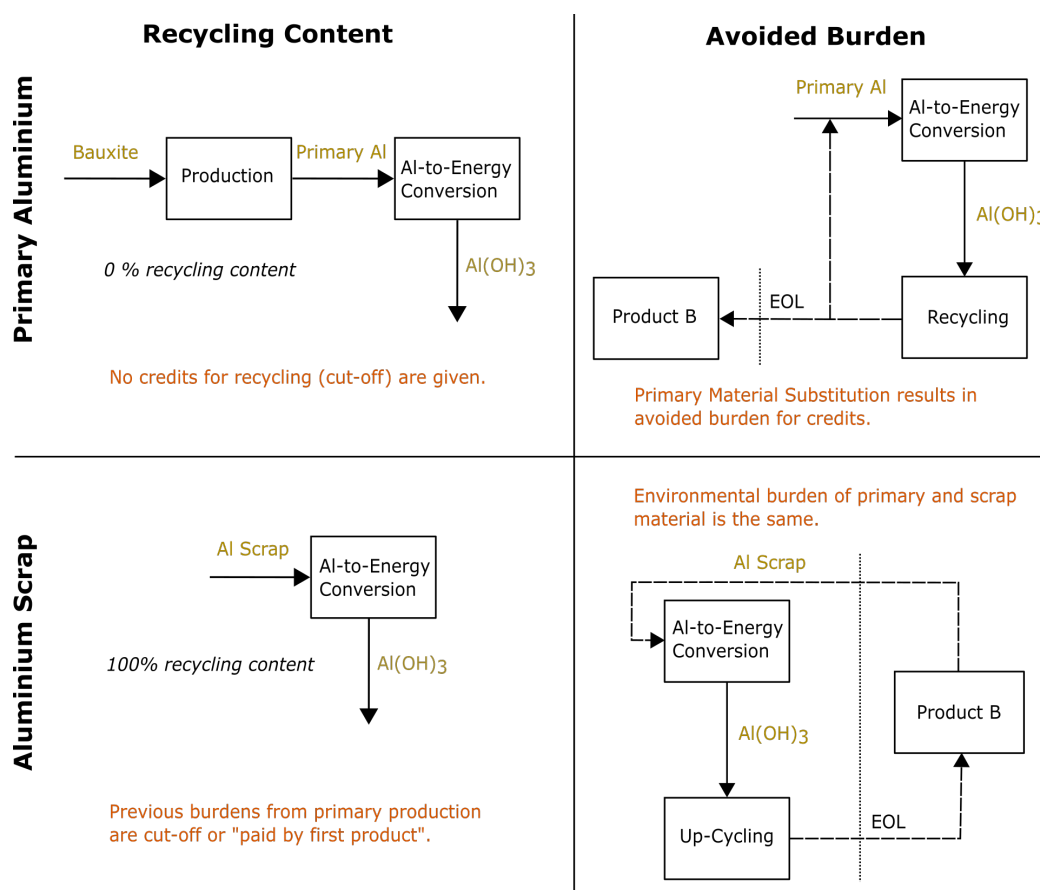


Figure 6.1: LCA allocation methods applied to the Al-to-Energy conversion process. The recycling content approach (left) shows both extreme options, 0 % recycling content from the primary aluminium source (upper part) compared to 100 % recycling content from aluminium scrap (lower part). No burdens are given for scrap consumed, but also no credits are given for recyclable materials generated by the Al-to-Energy system when using the recycled content approach. The avoided burden approach (right) includes the recycling of aluminium. At the end-of-life (EOL) the aluminium hydroxide is recycled or up-cycled to primary aluminium and re-used in other product systems resulting in a credit.



It is important to note, once the EOL of the Al-to-Energy conversion is reached; the aluminium leaving the system boundary is of high quality and can be used in other products, so the initial burdens of the resource extraction for the Al-to-Energy conversion will be credited by the avoided burdens of the next product. Comparing both options of the avoided burden approach, it becomes clear that only aluminium hydroxide which is lost from the system needs to be replaced and accounted for by the resource extraction of bauxite ore (primary aluminium source) or additional aluminium scrap input.

An internal review of the datasets at SPF further confirmed correct allocations and the completeness of the dataset.



Annex B: Description of process steps for LCA analysis

B.1.1 Calcination

Hydrate alumina crystals are heated to temperatures of around 1000 °C in the calcination process. The heat in the calciners drives off combined water leaving alumina deposited. A smelter-grade alumina will typically have an α -aluminium oxide content of about 5 % [20]. For the LCA it was assumed that this process heat is produced renewable electricity with a 100 % electricity to heat efficiency.

B.1.2 Inert Electrode Smelter Process

Since 1886 primary aluminium is produced by the electrolytic reduction of alumina (Al_2O_3), dissolved in a molten bath of sodium aluminium fluoride (cryolite), at a temperature of approximately 960 °C, by the Hall-Héroult process. In general, the electrolytic process occurs in steel cells lined with carbon [21]. A carbon block (mainly made of petroleum coke) forms the anode, which is consumed and converted to carbon dioxide (CO_2) due to the anode reaction ($3 \text{ C} + 6 \text{ O}_2^- \rightarrow 3 \text{ CO}_2 + 12 \text{ e}^-$). However, if the carbon anode is replaced with an inert material, these direct GHG emissions from this process can be reduced to zero. In this new process, inert electrodes extend into the cell and serve as anodes, whereas the carbon lining of the cell is the cathode, or wettable cathodes of TiB_2 are used as the cathode in order to further increase the efficiency of the process. Liquid aluminium is produced at the cathode, while oxygen is released at the anode. Aluminium fluoride (AlF_3) is added to neutralize the sodium oxide present as an impurity in the alumina. The AlF_3 content of the bath is significantly in excess of the cryolite in modern plants. However, inert anode processes have been proposed in combinations with electrolytes at much lower temperatures (700 – 800 °C), and sometimes also increased concentrations of potassium in the bath. The fluoride-containing electrolyte will still generate hydrogen fluoride, HF (g) and vaporization of NaAlF_4 (g) will continue, as determined by the composition and temperature of the electrolyte [22]. In addition, potassium may be lost from inert anode electrolytes. Fume gases are passed across a bed of alumina, where HF and NaAlF_4 are absorbed and thus re-introduced as much as possible into the process.

Cells equipped with inert anodes will not emit any CO_2 and CO from the anode reaction of the electrolysis process. Likewise, there will be no emissions of CF_4 and C_2F_6 , because carbon anodes are eliminated. Furthermore, emissions of PAH (from coal tar pitch used in the anodes, and particularly in Söderberg anodes) and sulphur compounds, mainly SO_2 (from sulphur compounds in the carbon anode raw materials) will be eliminated too. Nevertheless, current cells require a sufficient heat loss through the side and end walls to maintain a ledge of frozen electrolyte in order to protect the wall materials against the corrosive action of circulating electrolyte and metal. If the cell design and advanced material are not adjusted, this heat loss will be necessary also with inert anodes [23]. Solheim [24], Kvande et al. [23], Kovács et al. [22], and Gupta and Basu [25] point out, that an inert anode smelter process requires more energy due to the loss of enthalpy from the carbon anodes in order to maintain the heat balance. Even if the required heat loss can be reduced, retrofitting existing cells with inert anodes will require 1 kWh/kg Al more electricity compared to carbon anodes. Therefore, retrofitting existing cells with inert anodes will result in higher electric energy consumption. Solheim [24] critically compares carbon and inert anodes and suggests an energy consumption



of 14.9 kWh/kg Al for inert anodes, if current cells are retrofitted. Other authors even present higher values such as 16 kWh/kg Al [22]. The minimum theoretical energy requirement for inert anode cells is 9.18 kWh/kg Al. The required amount of energy is a crucial factor in this case and the environmental impacts are highly affected by the source of electrical power. Therefore, Gupta and Basu [25] conclude that in order to reach the full potential of inert anodes, this technology needs to be implemented with a vertical cell configuration (inert anodes and wettable cathodes) rather than retrofitting existing cells. This study assumed an inert smelting process using wettable cathodes with an energy consumption of 13.2 kWh/kg Al [26], corresponding to a smelting efficiency of 65 %.

Inert anode Al smelting has been tested in small scale by various research teams [11,27], and scale up of the process has been announced by Elysis, a joint-venture of RioTinto and Alcoa, that is currently constructing a 450 kA cell in its Alma Smelter⁷, and also by RUSAL⁸. However, there is no official data yet on the efficiency or electricity use of these smelters.

B.1.3 Casting

After the electrolysis, molten aluminium from the electrolytic process is tapped from the reduction cells, weighed, sampled and analysed before it is poured into a holding furnace and the temperature is controlled to approximately 750 °C. At this stage, the metal is refined to remove impurities such as sodium, magnesium, calcium oxide particles and hydrogen. This refining stage is performed by fluxing salts and the injection of a gas mixture into the molten metal, usually in an in-line reactor, before the casting takes place. The treatment gas used varies depending on the impurities. Slabs, T-bars or billets are cast in vertical direct chill casting machines that use water-cooled metal moulds and a holding table at the bottom part of the moulds. The table is lowered as the ingot is formed. Other casting methods include the use of metal moulds (static or continuously moving), continuous casting of thin sheets and continuous casting of wire rod. Additional small quantities of skimmings are also produced at this stage and are removed from the surface of the molten metal (dross) [28].

For the LCA analysis, it was assumed that 100% renewable (PV) electricity is used for this process.

B.1.4 Fabrication

Aluminium in the form of chips can be obtained from various cutting processes such as milling, lathe, sawing, drilling, cutting and grinding. Typically, each process produces different chip geometries.

B.1.5 Al-to-Energy Conversion

In air or water, a dense protective oxide film is formed easily on the aluminium surface. This film is passive in the neutral aqueous solution, but it can dissolve in an alkaline aqueous solution. Based on the reaction presented in Eq. 2 (section 2.2.1).

⁷ <https://elysis.com/en/carbon-free-aluminium-smelting-a-step-closer-elysis-advances-commercial-demonstration-and-operates>, accessed Nov. 5th, 2021.

⁸ <https://rusal.ru/en/press-center/press-releases/rusal-and-ball-corporation-partner-to-produce-ultra-low-carbon-aerosols>, accessed Nov. 5th, 2021..



A theoretical maximum of 0.111 kg of H_2 can be produced from each kg of Al. The maximum amount of heat that can be expected from a reaction at 60 °C ($\Delta H_r, 333 = -879$ kJ/mol) is 4.53 kWh (16.306 MJ) per kg Al [26]. It is assumed that only a minor amount (3 %) of Al is lost during each energy cycle, and these losses have been attributed to the produced $Al(OH)_3$ for this study, though the exact loss rate at this stage of development is unknown. Sodium hydroxide used to dissolve the protective oxide film of the aluminium source can be recycled within the system or at the end-of-life. Loss of NaOH was assumed to be a certain percentage (3, 5 and 10%) of the 6 M solution, the amount of 6 M solution being calculated based on the amount of water needed for the stoichiometric reaction of Al to $Al(OH)_3$.



Annex C: Requirements for "smelter grade" alumina

Table 6.2: Requirements for alumina used in smelters for aluminium production via Hall–Héroult process, the major industrial process for smelting aluminium.

Compound	Required value (%)	Typical value (%)
Al₂O₃	98,6	99
SiO₂	< 0,030; <0,02*	0,010
Fe₂O₃	< 0,030; <0,015*	0,010
TiO₂	< 0,005	0,002
Na₂O	< 0,400	0,330
ZnO	< 0,010	0,005
CaO	< 0,040	0,020
P₂O₅	< 0,001	0,0005
V₂O₅	< 0,005	0,001
MnO	< 0,002	< 0,001
Ga₂O₃	< 0,012	0,008