

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

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Abstract

Renewable metal fuels have great potential to act as a sector coupling seasonal energy storage. Renewable electricity can be generated in summer, transformed and stored in a metal fuel without losses as long as desired, and can provide decentralized heat and electricity at any time and any place. Aluminium as an energy carrier is of interest due to its high volumetric energy density ($> 23 \text{ MWh}\cdot\text{m}^{-3}$). Therefore, the production of heat and hydrogen from seven different aluminium recycling streams was analyzed and a conversion efficiency of close to 100% was reached for all of them. However, some of the obtained solid reaction products showed metal impurities, which require a purification process in order to close the material cycle. The concept provides a seasonal energy storage solution with "storage" costs in the range of 90 Euro per MWh. Additionally, life-cycle greenhouse gas (GHG) emissions of all studied aluminium-redox-cycles were substantially lower when compared to natural gas mini CHP plants.

Keywords: Seasonal Energy Storage, Renewable Metal Fuel, Aluminium Energy Carrier, Aluminium Recycling, Sector Coupling

1. Introduction

The storage of large quantities of renewable energy over long periods (more than three months) is still an important unsolved issue of the energy transition. In Europe, energy security and resource dependency have gained new urgency, partly as a result of the geopolitical situation and associated reduction or shutdown of natural gas and oil imports from Russia. Energy prices have reached record levels across Europe and might rise further as the winter approaches. Today, renewable electricity and heat from solar energy can be produced at low-cost and can, in combination with a short-term storage, even fulfill daily demand profiles of households, in particular during the summer. Nevertheless, when people need to heat their buildings in winter, additional energy sources or a seasonal storage is required. In this regard, renewable metal fuels can offer a simple, safe, and efficient solution. If excess "summer" energy is converted into chemical energy carriers, which can be stored without losses over several months, it can easily fill this winter gap and reduce or eliminate the dependency on fossil fuels. Aluminium, in particular, is a very promising renewable metal fuel candidate (Trowel et al., 2020).

Based on a sector-coupled aluminium-redox-cycle concept (Figure 1), electricity from solar or other renewable sources can be used in a storage charging process to reduce aluminium oxide or aluminium hydroxide into elementary aluminium (Power-to-Al). This reduction process is carried out via the calcination and/or inert anode smelter process which emits only O_2 (CO_2 -free Al smelter). In the storage discharging process, aluminium can be oxidized (Al-to-Energy) releasing hydrogen and heat, while again obtaining the by-product aluminium hydroxide at a reaction temperature below $280 \text{ }^\circ\text{C}$ or aluminium oxide at higher temperatures. The hydrogen can be electrochemically converted with a fuel cell system and the heat from both exothermal reactions (oxidation of aluminium as well as oxidation of hydrogen) can be used in buildings for the supply of domestic hot water and space heating. Therefore, aluminium acts as a seasonal renewable energy carrier with an energy recovery of more than $23 \text{ MWh}\cdot\text{m}^{-3}$ if it is stored as a solid block or, more realistically, $15 \text{ MWh}\cdot\text{m}^{-3}$ as a bulk storage material (e.g. Al grit). This concept can cover a significant amount of heat and electricity in winter when implemented in decentralized combined heat and power generation (CHP) systems (Haller et al., 2021).

Dudita et al. (2019) investigated the aluminium-water oxidation reaction in alkaline solutions ($\text{NaOH}_{(\text{aq})}$) with primary aluminium as a source material and showed that the reaction depends on various conditions. In particular, the particle size, shape, and quality of the aluminium can affect the reaction time and the precipitation of the by-product. However, from an economical point of view, potential low-cost aluminium recycling streams could be of interest. Therefore, different source material, including old scrap from post-consumer use, as well as new scrap

from the manufacturing process of semi-fabricated and final products, were identified and tested. The goal was to answer questions concerning the suitability of secondary aluminium source material and their effect from an economic and environmental point of view.

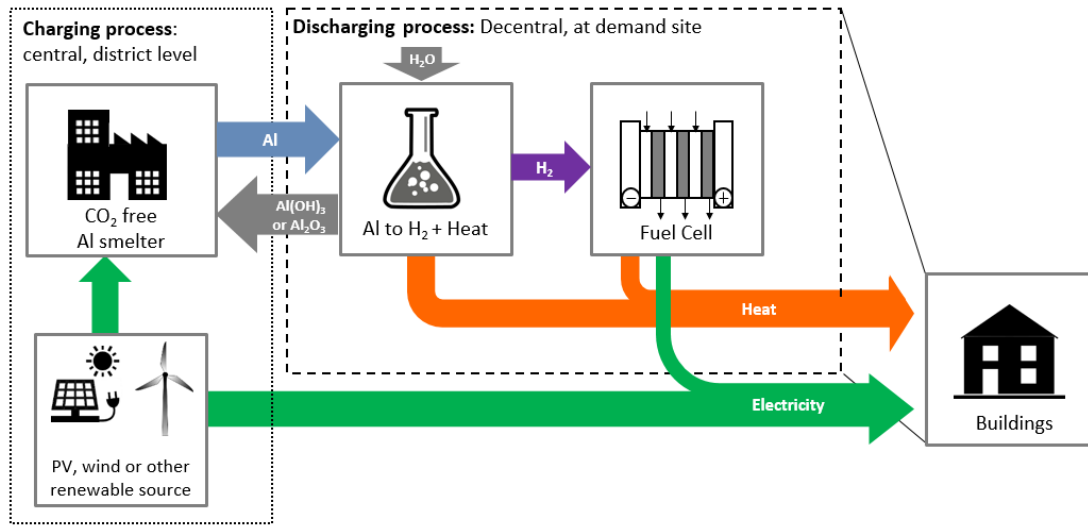


Figure 1: Overall sector coupling energy storage concept based on aluminium-redox-cycles, adapted from Haller et al (2019).

2. Procedure and methodology

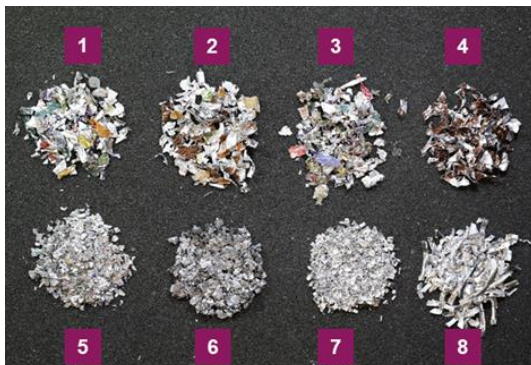


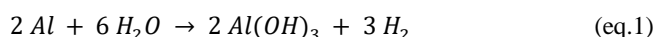
Figure 2: Visual aspect of the aluminium samples after cutting, shredding, cleaning, and drying.

To evaluate the suitability of secondary aluminium as a source material for the discharging process (oxidation reaction) and to assess the quality of the by-product and potential market applications, five aluminium materials from post-consumer use (sample 1 to 5 of Figure 2) and two new Al scrap samples from metal processing (sample 6 and 7) were selected. All samples contained various impurities, e.g. coffee residues, oil, surfactants, and other metals, and thus had to undergo a pre-treatment process before use. A pure aluminium reference (sample 8, class P1020) provided the baseline of the following chemical analysis.

2.1. Aluminium source material, pre-treatment and chemical analysis

Initially, a preparation process including cutting and shredding, cleaning and drying, as well as a thermal treatment for 30 minutes at a temperature of 550 °C, was implemented in order to remove unwanted non-metallic impurities as much as possible. In a next step, the prepared samples were chemically analyzed to obtain the elemental composition by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

To assess the completeness of the oxidation reaction, the efficiency and kinetics of each aluminium sample (prepared without thermal treatment) were studied at room temperature using a 6 M¹ NaOH_(aq) solution as a reaction promoter. The maximum amount of hydrogen that can be produced from the aluminium sample was calculated according to eq. 1.



Finally, aluminium hydroxide (Al(OH)₃) was obtained as a solid reaction product (from aluminium samples without thermal treatment) in a 6 M NaOH_(aq) solution at a stable reaction temperature from 60 to 70 °C.

¹ The molarity (M) is defined as the number of moles of solute dissolved in one liter of solution.

The $\text{Al}(\text{OH})_3$ was separated via vacuum filtration and washed until the pH of the filtrate decreased from 14 to 7. Before all samples were chemically analyzed via X-ray fluorescence (XRF) analysis, a thermal treatment for 1 hour at 1050 °C was implemented. In this case, the remaining dry mass can be associated with the presence of metal oxides.

2.2. Global Warming Potential (GWP)² and energy cost

The potential environmental advantages of the aluminium-redox-cycles were evaluated using the standardized procedures of LCA as per ISO 104040 (2006) and ISO 104044 (2006), which determine the environmental impact associated with the concept from resource extraction to end-of-life burdens. 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). For this study, life-cycle GHG emissions and their associated impacts on climate change are used as the main indicators for the environmental performance of the aluminium-redox-cycles. All GHG emissions were assessed by the IPCC 2013 GWP 100a V1.03 method using the Ecoinvent database version 3.1. In addition to the background process of the PV electricity production from the Ecoinvent dataset, the updated life cycle inventory data set from Frischknecht et al. (2020) was also applied.

For the economic assessment, current world market prices or specific estimates from the industry were used. In general, two different cases can be distinguished for the use of recycling / scrap material for the aluminium-redox-cycles.

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

It should be noted that the closed cycle is dependent on the question whether the produced aluminium hydroxide or alumina is suitable for the inert anode smelter, and the open cycle is dependent on the question whether there will be any market and demand for the resulting by-product.

3. Results and Conclusion

3.1. Aluminium source material, pre-treatment, and chemical analysis

Results of the ICP-OES measurement identified iron as a metallic impurity in most samples. Sample 5 and 6 had a wide range of other impurities including Mg, Mn, Zn, Cu, Co, Cr, and Ni (Table 1).

Table 1: ICP-OES results indicating the aluminium content and the presence of 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		0.03						
2	5.0	97.6		0.05						
3	4.9	97.1		0.04						
4	5.0	99.6		0.05						
5	4.7	88.6	0.07	0.21			0.04	0.03	0.02	
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						
8	5.3	99.7								

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

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).

Based on the analysis presented in Table 1, the aluminium content in the samples could be identified in the range of 63 to 93% (including weight losses from thermal treatment).

The analysis of the completeness of the reaction showed that some samples with metallic impurities (i.e., strong presence of elements other than aluminium) produced more hydrogen than could be expected from its aluminium content alone (Figure 3). The primary aluminium sample 8 (99.7% purity) produced 99 to 100% of the expected hydrogen. However, sample 6, which contained large fractions of iron and other elements, reached 142% of the theoretical value based on the aluminium content. Therefore, it is very likely that metals other than aluminium have reacted with water and produce hydrogen (Yavor Y. et al., 2015).

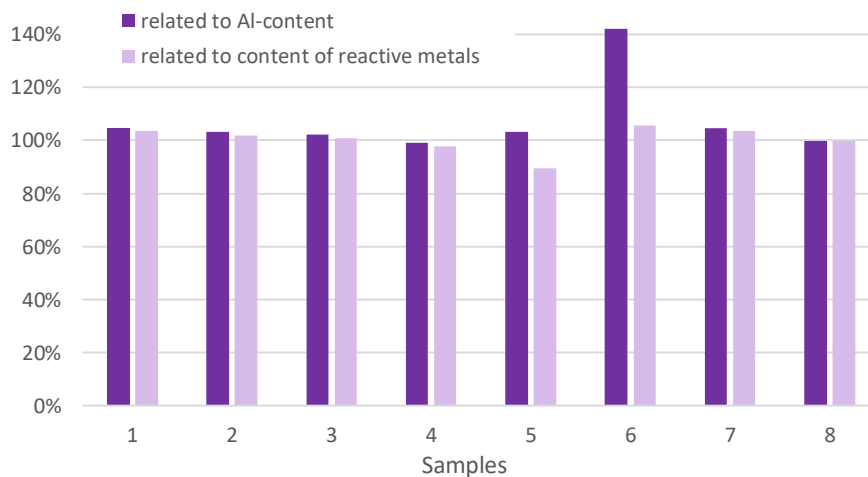


Figure 3: Completeness of the H₂ evolution reaction based on the max. theoretical H₂ production from Al content.

The XRF analysis of the aluminium hydroxide identified a considerable amount of sodium (Na₂O) in all samples with concentrations mostly below 2% (wt./wt. after subtraction of ignition losses (LOI)). This amount of sodium, present in the aluminium hydroxide after rinsing with water, indicates that about 6 to 10%³ of the used NaOH for the reaction ends up in the aluminium hydroxide. Furthermore, most samples contained a considerable amount of iron, some magnesium, and, to a lesser extent, manganese, silicon, and zinc. These findings lead to the conclusion that for most samples (especially old scrap material) an additional treatment and purification step would be necessary in order to recycle them in a conventional aluminium smelter for a closed cycle application. Thus, it can be assumed that the market value of the obtained aluminium hydroxide is rather low. In case of an open cycle implementation, a market has to be identified or created. So far, there doesn't seem to exist an industrial process which would allow a direct application of the obtained alumina without further purification steps.

3.2. Global Warming Potential (GWP) and energy cost

Based on the LCA that used the avoided burden approach, it could be established that the selection of the source material (secondary vs. primary aluminium) had only a minor influence of 1 to 2% on the estimated total GHG emissions of the aluminium-redox-cycles. The same can be concluded for the sodium loss rate, which was varied from 3 to 10%. However, the GWP of the electricity (upstream supply chain) used in the aluminium inert electrode smelter process, as well as the renewable energy input to produce the required heat for the calcination process (forming alumina from aluminium hydroxide), had a significant influence, and accounted for more than 80% of the total estimated life cycle GHG emissions. 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 g CO₂eq/MJ_e. The recently published new datasets from Frischknecht et al. 2020, on the other hand, assess GHG emissions of approx. 8.9 g CO₂eq/MJ_e (with a yield of 975 kWh/kW_p) for the electricity

³ The percentage is 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 data of the aluminium hydroxide produced indicated 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.

production from PV for an average Swiss PV module supplier mix from 2019. The main reason for the overestimation of the GWP in the Ecoinvent dataset is caused by outdated electricity mix data used in the production of the PV modules. Thus, the estimated total GWP for the aluminium-redox-cycles range from 48 g CO₂eq/MJ to less than 25 g CO₂eq/MJ of energy (hydrogen and heat) produced.

In order to compare the GWP of heat and electricity produced from the discharging process with an alternative mini CHP plant, a PEM fuel cell system was added to the system boundary with an electric efficiency of 50% (HHV), and 45% to heat efficiency. Providing heat and electricity from a natural gas micro-CHP unit (2 kW_e with a fuel to electric efficiency of 25% based on HHV and a total efficiency of 85%) is linked to a GWP of approx. 83 g CO₂eq/MJ (Figure 4). In comparison, a reduction of GHG emissions of 33 to 64% per MJ can be achieved by the aluminium-redox-cycles. Furthermore, 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, an overall GHG emission reduction of over 80% is possible.

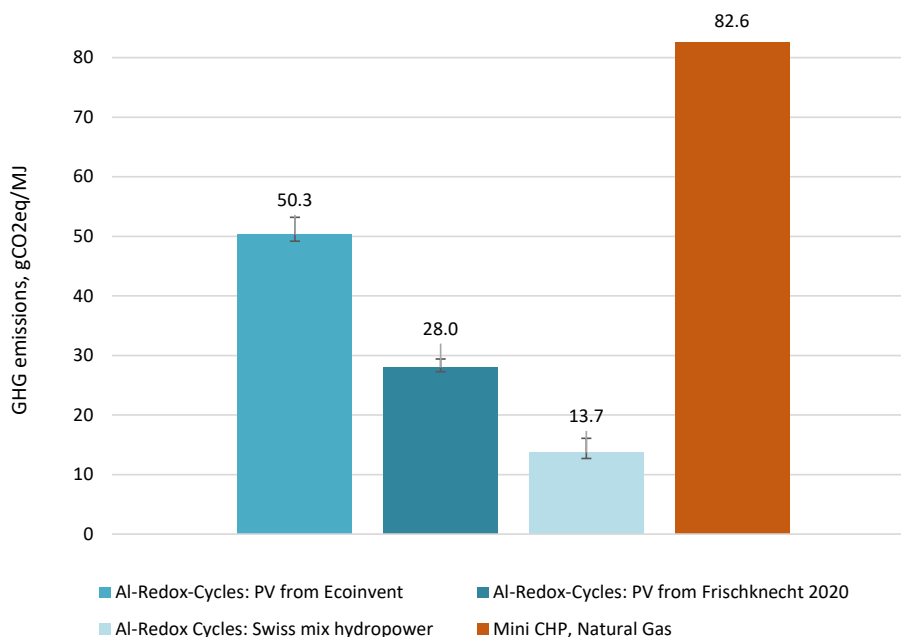


Figure 4: Average total life cycle GHG emission per 1 MJ of electricity and heat produced using primary and scrap aluminium as the source material (min. and max. values are indicated by the error bar). The results are based on PV electricity from Ecoinvent "photovoltaic, at plant/CH" (21 gCO₂eq/MJ_e), and values by Frischknecht et al. (2020) (8.9 gCO₂eq/MJ_e) as well the Ecoinvent Swiss mix of electricity production from hydropower (1.3 gCO₂eq/MJ_e). Size of mini-CHP plant: 2 kW_e.

The cost of primary aluminium and high quality (smelter grade) Al(OH)₃ (2'000 and 187 Euro per metric ton, respectively) were based on the past five years of market history. It was assumed that the low quality Al(OH)₃, containing many metal impurities, can be added into the Bayer process instead of Bauxite ore and thus giving a market price similar to the present market price for Bauxite ore (45 Euro per metric ton). Therefore, depending on the value of the aluminium source material, the quality of the obtained Al(OH)₃, and the material flow scenario (open or closed cycle), a wide range of potential net material costs, i.e., cost of purchase minus revenue from the sale of Al(OH)₃, were estimated:

- High value scrap; High quality Al(OH)₃: **11 Euro/MWh** (closed cycle) and **129 Euro/MWh** (open cycle)
- Low value scrap; Low quality Al(OH)₃: **2 Euro/MWh** (closed cycle) and **26 Euro/MWh** (open cycle)
- Low value scrap; High quality Al(OH)₃: **0.4 Euro/MWh** (closed cycle) and **-20 Euro/MWh** (open cycle)

The results indicate that the net material cost per MWh of energy produced from aluminium ranges between -20 and 130 Euro/MWh. However, these cost assumptions do not include any additional process steps for purification of material and thus do not present the full cost. Furthermore, for the closed cycle, the cost for the aluminium smelting would have to be added.

In general, aluminium “storage” costs in the range of 90 Euro/MWh can be expected for a Power-to-Al plant operating 2920 h per year. Not included in this storage cost are electricity input, transport of the material, and the conversion of aluminium back to energy in decentralized units (discharging process).

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