Circular Use of Aluminium as an Energy Carrier

Hüseyin Ersoy[1], Manuel Baumann[2], Marcel Weil[3], Stefano Passerini[4] and Linda Barelli[5]
1. PhD student
2. Researcher and deputy research group leader
Institute for Technology Assessment and System Analysis (ITAS), Karlsruhe Institute of Technology, Karlsruhe, Germany
3. Dr.-Ing, Head of research group
4. Professor, Director
Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Karlsruhe Institute of Technology, Ulm, Germany
5. Associate Professor
University of Perugia, Perugia, Italy
Corresponding author: hueseyin.ersoy2@kit.edu

Abstract

Aluminium (Al) is a functional material and it has a critical importance for the sustainable transition in many sectors. Besides its use in the manufacturing Al is a dense heat and hydrogen (H_2) carrier which will create additional business cases for its use with the energy transition. In this study, a business case for the use of Al as energy carrier is introduced. An Al-based system design is introduced and its techno-economic implications are presented based on a computer model. Environmental sustainability hotspots are identified and emerging solutions are introduced. The results provide high motivation for the further research of Al as an energy carrier depending on the achieved high overall conversion efficiency, degree of flexibility, and potentially cheap Al-based H_2 price.

Keywords: Aluminium, Hydrogen, Power-to-X, Circular economy.

1. Introduction

Environmental challenges due to the climate change necessitates strict emission reduction measures and more sustainable concepts in every aspect of our daily life. In this manner, considering the contribution of the fossil fuelled energy generation and transportation sectors on the total greenhouse gas emissions (GHGs), a green transition of the energy sector with the aid of renewable energy technologies, sustainable and carbon-neutral fuels are in progress. Additionally, a major challenge is the criticality of raw materials associated with concerns regarding supply risk, scarcity, and import reliance [1]. In order to meet the growing demand, supply of metals with highly efficient, sustainable and clean processes starting from mining to delivery of the manufactured goods is inevitable to realize such a transition. The concerns regarding raw material criticality suggests the usage of application potential of abundant metals that are produced in large quantities with a long term ensured availability such as Al. Al is a functional material with its high thermal and electrical conductivity, low density, ductility, and non-ferromagnetic behaviour. Hence, Al has a wide application spectrum in manufacturing technologies and products necessary for a sustainable transition such as batteries, fuel cells, motors, wind turbines, photovoltaics, robotics, drones, 3D printing and Information and Communication Technologies (ICT) [2]. Besides manufacturing applications, the use of Al as an energy carrier is an emerging topic that is discussed in this paper. Recent studies refer to the use of Al as a renewable energy storage medium thanks to its high volumetric heat storage capacity and water-splitting behaviour due to high reactivity which produces hydrogen (H_2) [3–8]. Using Al as an energy carrier is not an entirely new concept it has been used as an additive in propellants since over 60 years [9]. But using such a dense energy carrier and vastly available metal as a renewable energy carrier is a new concept developed with the energy carrier and storage demand of evolving global energy system. Noting that, primary Al is an energy intensive metal and its production causes direct Green House Gases (GHG) emissions, and some hazardous wastes including the pre-supply chain. Advances in the technological development and implementation of sustainability measures in the Al industry brings also some opportunities creating new business cases. Nevertheless, all these advances require decarbonization of the aluminium supply chain and the establishment of a circular economy without increasing the additional demand on bauxite mines. The energy transition implies potential advantages, but also some challenges for primary Al production, which needs to be addressed. In the following, these challenges will be identified and a circular concept will be introduced for a sector-coupling case between Al smelters and energy generation sectors.

2. Use of Aluminium as an Energy Carrier

2.1 Primary Aluminium Production Process and Sustainability Hotspots

The European Al demand is showing a rapid increase due to the increasing demand in every technological field. Major Al consuming sectors are identified as transport (27 %), construction (24 %), and packaging producers (15 %) [10]. Especially, the demand of the transportation sector is forecasted to increase 55 % with respect to the 2017 [10]. Thus, it is very important to secure the supply chain, increase resource and energy efficiency, and implement decarbonization measures through the entire chain. Al appears in the nature as bauxite ore, which consists of gibbsite ($Al(OH)_3$), boehmite (ϒ-AlO(OH)), and diaspore (α-AlO(OH)) minerals. Considering the geographical distribution of high-quality bauxite mines, Europe highly depends on the imports (74 % of total consumption) from Guinea, and Brazil. Only a very small share of bauxite is mined in Greece and to lesser extent in Hungary that sums up 2.3 million tonnes (12 % of total consumption) resulting overall 87 % import reliance as reported by European Commission [11]. The most important use of bauxite is aluminium production, due to high import reliance and extraction stages, it is classified as a critical material for Europe [2]. To decrease the dependency on bauxite a higher circularity of Al in the technosphere is necessary. Consequently, mined bauxite needs to be refined. It is then transported to aluminium oxide (Al_2O_3) producers. (see Figure 1) Al_2O_3 is the parent material that Al is reduced from and it is produced via the so-called Bayer process. The Bayer process is comprised of two subprocesses where the bauxite ore is treated with caustic soda in order to extract the gibbsite and extracted gibbsite then calcined at 1 100 °C to precipitate Al_2O_3 [12]. The full process requires 412 kWh electricity and 496 Nm^3 of natural gas per tonne of Al_2O_3 in a modern state-of-the-art plant, where standard process plants consumes around 26 % more natural gas (sum of energy consumed in pressure leaching, crystallization, rotary kiln, and calcination) [13]. The process doesn't require large amount of electricity with respect to the smelting process. European production and imported (from Jamaica, Surinam, and Brazil) Al_2O_3 is then transported to smelting facility for producing primary Al. The process is an electrolytic reduction process reducing Al_2O_3 to Al. The electrolysis takes place in a cryolite (Na_3AlF_6) - Al_2O_3 mixture bath. It is an energy intensive process consuming 14.1 kWh_{AC}/kg_{Al} of electricity on global average [14].

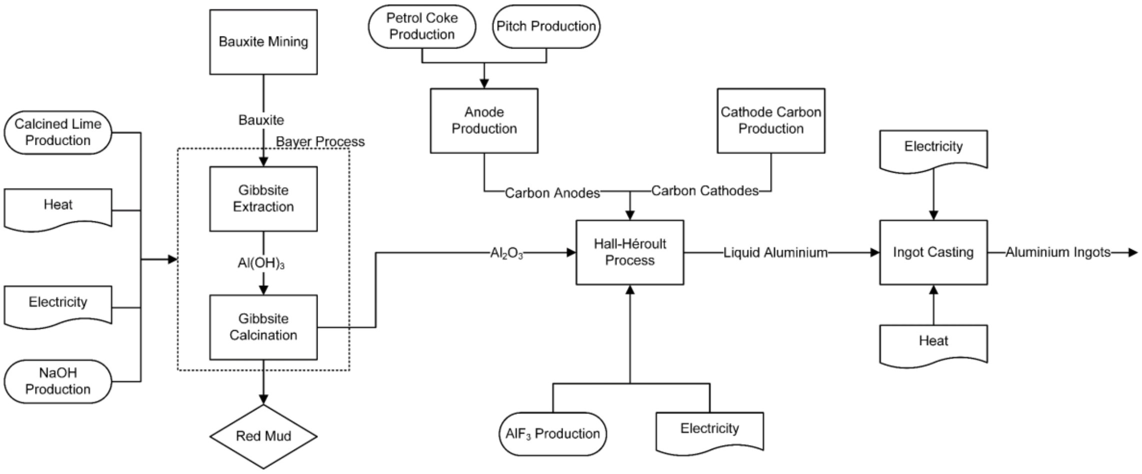

Figure 1. Primary aluminium supply chain involved process and materials. (Own figure based on [15])

Hence the environmental impacts can be reduced to some extent via implementation of carbon-free heat and electricity sources. Following the process order, given environmental sustainability hotspots can be identified. The waste red mud of the Bayer process is considered very problematic from environmental perspective since it is highly alkaline and its heavy metal constituents contaminate the air and soil. The red mud consists of Fe_2O_3 (42.3 %), Al_2O_3 (16.3 %), CaO (11.6 %), SiO_2 (7 %), TiO_2 (4.3 %), Na_2O (3.8 %), La_2O_3 (0.09 %), CeO_2 (0.06 %), Sc_2O_3 (0.02 %), Nd_2O_3 (0.01 %), Y_2O_3 (0.01 %), ignition losses (12.66 %) and others (1.85 %) [16]. In the current practice red mud is not properly treated but stored in big mud lakes. In theory, since the red mud consists of many metal oxides it could be refined and oxides can be extracted. To reduce the environmental burdens, sustainable re-vegetation and residue management, neutralization of red mud using mineral acids, acidic waste (pickling liquor waste), coal dust, superphosphate and gypsum as amenders, CO_2 sequestration, sintering with silicate material, geopolymers and seawater are studied techniques in the literature for further use and treatment of the red mud [17–19]. One novel concept introduced in [20] proposes direct transformation of red mud into pig-iron and mineral wool using an electric arc furnace (EAF) that could also increase the resource efficiency. In the Hall-Héroult process electrodes are made of carbon that Al is separated from its oxide. As a result, separated oxygen recombines with consumed carbon anodes and yield direct CO_2 emissions. Furthermore, the fluoride is also recombined with the carbon that result in perfluorocarbon (CF_4, 7 390 kg_{CO2} eq.) and hexafluoroethane (C_2F_6, 12 200 kg_{CO2} eq.) emissions [21]. All direct emission related aspects are the main challenges that requires innovative and sustainable solutions. As a solution for avoiding the side reactions taking place during the electrolysis inert anode and cathode electrodes are presently the most promising solutions. With the implementation of inert anodes, it is possible to avoid emissions since the electrode and electrolyte materials do not recombine with the released oxygen [22]. World leading Al producers already reported some operational experience in some pilot cells using inert anodes [23]. Additionally, some aluminium producers are trying to improve the energy performance of their cells such as Norwegian Hydro Aluminium company has reported an energy consumption of 11.5–11.8 kWh/kg_{Al} on their pilot scale industrial plant using conventional carbon anodes [24-26]. Hence, considering proposed solutions for the addressed concerns, Al has a potential to be produced carbon-free in the future. An established carbon-free Al production and supply chain will open the door for new opportunities for Al to be used in different applications. In the following, as an example of future business opportunities use of Al as an energy carrier is explained.

3. Use of Aluminium as Circular Metal Fuel

Metals tend to lose electrons and react due to their electronegativity; this tendency is explained as reactivity. All reactive metals are dense energy carriers, and they react with oxygen and water spontaneously, this spontaneous exothermic reaction yields large amount heat and/or H_2 based on the oxidizer type [27]. This can be also carried out by electrochemical conversion as batteries operate based on redox principle. Both conversion mechanisms have its specific advantages and disadvantages. For example, the electricity surplus from the renewable energy generation can be stored in batteries (which relies on critical materials) or it can be used for producing synthetic fuels and H_2 production with less efficiency. Alternatively, the energy surplus can be used for producing metals. With the increasing concerns regarding the scarcity and supply criticality of the used metals in energy storage field, abundant metals such Al, magnesium (Mg), sodium (Na), and zinc (Zn) became more attractive to be used as energy carriers [28]. In this context, metals such as Al and Fe have remarkable aspects that motivates technology developers for the further use of these metals. Especially, large production rate, convenient cost, outstanding volumetric energy density (see Table 1), infinite recyclability, well-established production and supply chain are the main motivating aspects.

Table 1. Energy density of various energy carriers [5].

Energy carrier	Gravimetric energy density [kWh/kg]	Volumetric energy density [kWh/liter]
B	16.4	38.3
Li*	12.7	6.8
Al	**8.6**	**23.5**
Fe	2.1	16.7
Na	5.9	5.7
Mg*	7.3	12.6
Si	9.1	22.5
Ammonia (Liquified)	5.2	3.2
LNG	14.9	6.2
H_2 (Liquified)	33.3	2.3
H_2 (@ 700 bar)	33.3	1.4

*Critical materials according to the EU's critical materials list.

Based on this motivation, metals such as Al, Fe, and Na are the most convenient metals with improving sustainable production methods. For instance, as an alternative renewable energy carrier for storing the excessive renewable generation iron combustion system is also introduced on pilot-scale with anticipated carbon-free steel-making process [29]. The operation principle of combusting Fe particles is to produce electricity using the released thermal energy. Noting that Al provides superior properties in terms of energy density, similar approaches are also investigated since it has a large carbon-neutrality potential. Both electrochemical and thermochemical conversion of Al are very promising techniques. The electrochemical conversion of Al in rechargeable batteries faced some technical difficulties mainly due to its negative reduction potential which reduces the energy density of the system [30]. Nevertheless, recently a consortium of Israeli and Indian battery manufacturers introduced mechanically rechargeable Al-air batteries to be used in automotive applications. Hence, current state of the suitable electrolyte and cathode materials enable use of Al-air batteries, oxidized Al (in form of Al_2O_3 or $Al(OH)_3$) needs to be removed and recycled to Al after the battery is discharged [31]. Perhaps, use of mechanically rechargeable batteries are lacking operational practicability for mobility applications but use of these batteries on large scale for long-term energy storage appears to be a more feasible approach. In addition to the electrochemical conversion, two mechanisms employing the combustion of Al have been studied in the literature so far, these are the wet and dry combustion processes expressed with the following reactions [5]:

$$4Al + 3O_2 = 2Al_2O_3 \ (\Delta H = -8.6 \text{ kWh/kg Al}) \quad (1)$$
$$2Al + 3H_2O = Al_2O_3 + 3H_2 \ (\Delta H = -8.6 \text{ kWh/kg Al}) \quad (2)$$

The first reaction (Equation (1)) is an extreme thermal process and it requires an advanced combustion design [32]. Bai et al. [33] proposed replacing the combustion section of coal power plants with Al combustors and investigated its technical feasibility on a computational model. Their results stipulate high conversion efficiency and economic benefit besides difficulties in retrofitting the combustion section. Both reactions yield the same amount of energy, but the second reaction (Equation (2)) mechanism yields 4.16 kWh heat and 0.111 kg H_2 per kg of combusted Al [7,8]. The latter is more of interest considering the increased flexibility and versatility of the released energy. The generated heat can be used in a heat circuit to run a steam turbine for producing electricity. Produced H_2 can be used for various applications and electricity production as well as described in Ersoy et. al. [5]. Here a circular business case is proposed in general terms as an example by benefiting advances in the decarbonization of the Al supply chain as illustrated in Figure 2.

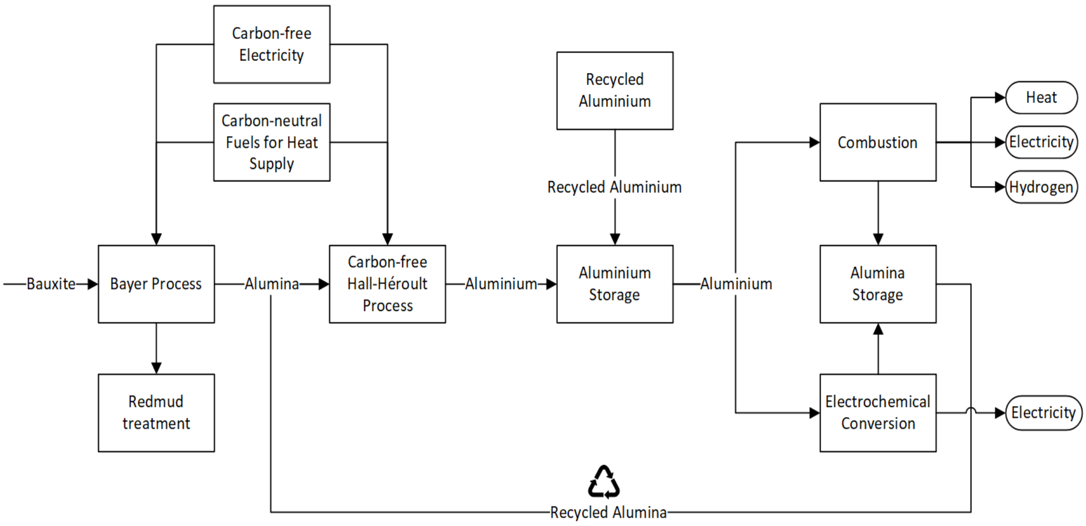

Figure 2. Aluminium production and energy sector coupling circular business case (Own figure).

The proposed circular business case, requires supply of carbon-free Al to the storage and to the energy generation site and collection of the combustion product (Al_2O_3) to produce Al with the excessive renewable energy from the grid. In this study, a combustion plant employing wet combustion is analysed within the given concept. The combustion plant proposed (see Figure 3) consists of an Al combustion chamber, a thermal circuit for cooling the combustion chamber, and a steam turbine for electricity generation using the heat from cooling. Additionally, a solid oxide fuel cell (SOFC), H_2 compressor, and gas turbine heat recovery sections are thermally integrated to the system. Here a phase separator is located for collecting the solid Al_2O_3 particles, the remaining flow is consisting of steam and H_2 mixture which is diverted to SOFC cell section for generating electricity. The rated power of the system ~4MW_e with an Al flow rate of ~275 g/s.

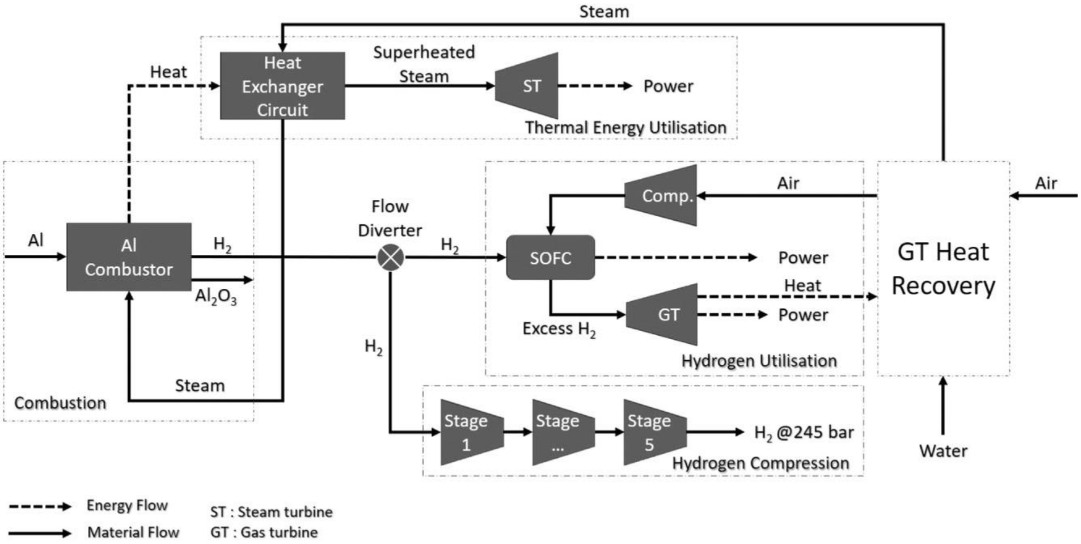

Figure 3. Simplified wet combustion plant layout [4, 5].

4. Techno-economic Evaluation Results

The system is designed in a way to enable the use of produced H_2 at varying operation loads of the fuel cell [4]. According to the thermal optimization results, the critical element for maintaining the thermal efficiency of the system is the SOFC, hence two partial operation loads are determined as 65 % and 80 %. This enables the use non-utilized H_2 for external use, providing 28–47 kg H2/h. The system proves overall 35.6–40.7 % Power-to-X (PtX) conversion efficiency considering an Al smelting energy intensity of 11 kWh/kg. This implies a higher conversion efficiency than any other Power-to-X alternatives except reversible H_2 SOFC system (48 %) using wind power [5]. Moreover, assuming various electricity prices (0–50 €/MWh_e) and Al prices (0.93–1.65 €/kg Al, allocating energy costs with the corresponding electricity prices and deducting the cost of Al_2O_3) the levelized cost of electricity (LCoE) varies in the range of 162–334 €/MWh_e for 4 000 equivalent annual full load hours (FLHs) [5]. The Al-based H_2 cost (LCoH) is estimated as 5.4–11.8 €/kg_{H_2} under same operational conditions [5].

5. Conclusion and Outlook

Herein, this work constitutes a preliminary techno-economic evaluation based on the anticipated developments in the Al industry. The findings of this investigation highlight the usability of Al as an energy carrier and depict a high techno-economic feasibility of such a circular concept. Considering the European energy scenarios, supply of the fuels for transportation and industrial sector will be mainly covered by renewable fuels, such as H_2, methane, and ammonia. However, use of Al as a renewable fuel is very competitive considering to overall conversion efficiencies. The preliminary assessment results imply that overall conversion of Al for re-electrification is more efficient than H_2 polymer electrolyte membrane (PEM) fuel cell and electrolyzer coupling system (in cavern storage) and the cost is very competitive as well on a MWh basis. But the advantage of the Al-based system is on-site production and storage of the power, unlike in cavern storage case. Regarding the fuel production costs even with the considered max Al price, Al-based H_2 is potentially cheaper than renewable methanol, kerosene (Fischer-Tropsch), and methane. But in almost in the same range with H_2 under same conditions. It is important to note that, in this system H_2 is produced as a by-product and it turned out that generation of H_2 from Al has a great techno-economic potential. Hence, a more simplified process without electrical conversion of the H_2 could yield cheaper Al-based H_2 prices. Use of Al as an energy carrier has outstanding benefits once a sustainable manufacturing chain will be established. To this aim following steps can be identified as the most critical obstacles regarding its sustainability aspects:

- Inefficient and non-green practices of bauxite mining,
- Use of fossil fuels for heat supply in all processes,
- Wasted materials within the red mud, and ecological concerns stemming from its treatment,
- Direct GHG emissions related to smelting process.

Once these problems are solved, Al could strongly contribute in the sustainability of other Al-intensive products. Even though, some actions require more efforts and depend on technological developments such as inert anodes and cathodes, some of these challenges related to the pre-chain of Al can be overcome with the circular economy approach. Simply starting with recycling of packaging materials, integrating such concepts will also create additional benefits. As an example, the introduced business case here depicts high potential on using Al as an energy carrier without increasing the mining demand of bauxite and providing a continuous use of the same amount in a closed-loop.

6. References

1. Magnus Gislev et al., *Report on critical raw materials and the circular economy*, (2018).
2. S Bobba et al., Critical Raw Materials for Strategic technologies and Sectors in the EU, *A Foresight Study, Luxembourg, European Union* (2020).
3. JM Bergthorson et al., Direct combustion of recyclable metal fuels for zero-carbon heat and power, *Applied Energy* 160 (2015), 368–382.
4. Linda Barelli et al., Reactive Metals as Energy Storage and Carrier Media: Use of Aluminum for Power Generation in Fuel Cell-Based Power Plants, *Energy Technology* 8 (9) (2020), 2000233.
5. Hüseyin Ersoy et al., Hybrid Energy Storage and Hydrogen Supply Based on Aluminum—a Multiservice Case for Electric Mobility and Energy Storage Services, *Advanced Materials Technologies* (2022).
6. KA Trowell et al., Aluminum and its role as a recyclable, sustainable carrier of renewable energy, *Applied Energy* 275 (2020), 115112.
7. Michel Y Haller et al., Seasonal energy storage in aluminium for 100 percent solar heat and electricity supply, *Energy Conversion and Management: X* 5 (2020), 100017.
8. Michel Y Haller et al., Combined heat and power production based on renewable aluminium-water reaction, *Renewable Energy* 174 (2021), 879–893.
9. MW Beckstead, *A summary of aluminum combustion*, Brigham Young Univ Provo Ut, (2004).
10. European Aluminium, *Vision 2050 - European Aluminium's Contribution to the EU's Mid-century Low Carbon Roadmap, European Aluminium*, (2019).
11. European Commission, Secretariat-General, Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions *The European Green Deal*, *European Commission*, Brussels, (2019).
12. Efthymios Balomenos et al., Energy and Exergy Analysis of the Primary Aluminum Production Processes: A Review on Current and Future Sustainability, *Mineral Processing and Extractive Metallurgy Review* 32 (2) (2011), 69–89.
13. Jürgen Vasters and Gudrun Franken, *Aluminium - Sustainability Information*, *Federal Institute for Geosciences and Natural Resources (BGR)*, Hannover, Germany, (2020).
14. Primary Aluminium Smelting Energy Intensity, *World Aluminium*, https://www.world-aluminium.org/statistics/primary-aluminium-smelting-energy-intensity/ (accessed on 12.08.2022).

15. Rolf Frischknecht et al., Life cycle inventory data and environmental metrics for the primary aluminium industry, *International Aluminium Institute*, (2017).
16. Gözde Alkan et al., A Mineralogical Assessment on Residues after Acidic Leaching of Bauxite Residue (Red Mud) for Titanium Recovery, *Metals* 7 (11) (2017), 458.
17. Suchita Rai et al., Treatment of alumina refinery waste (red mud) through neutralization techniques: A review, *Waste Manag Res* 35 (6) (2017), 563–580.
18. Yuancheng Li et al., Preparation of red mud-based geopolymer materials from MSWI fly ash and red mud by mechanical activation, *Waste Management* 83 (2019), 202–208.
19. Danielle Bonenfant et al., CO $_2$ Sequestration by Aqueous Red Mud Carbonation at Ambient Pressure and Temperature, *Ind. Eng. Chem. Res.* 47 (20) (2008), 7617–7622.
20. Efthymios Balomenos et al., EAF treatment for the efficient and complete exploitation of the bauxite residue (red mud) produced in the Bayer process, *Proceedings of the European Metallurgical Conference EMC* 2013, (2013): pp. 285–292.
21. A. IPCC, *IPCC fourth assessment report (AR4)*, IPCC, Vol. 1, 976, 2007.
22. Yong He et al., Recent progress of inert anodes for carbon-free aluminium electrolysis: a review and outlook, *J. Mater. Chem. A* 9 (45) (2021), 25272–25285.
23. Rio Tinto and Alcoa announce world's first carbon-free aluminium smelting process, *ELYSIS,* https://www.elysis.com/en/rio-tinto-and-alcoa-announce-worlds-first-carbon-free-aluminium-smelting-process (accessed on 12.08.2022).
24. Sébastien Becasse et al., APXe Cell Technology: 7 Years of Low Energy Operation, *Light Metals* 2018, 699–704.
25. Pierre Reny et al., Hydro's New Karmøy Technology Pilot: Start-Up and Early Operation, *in* L. Perander (Ed.), *Light Metals* 2021, 608–617.
26. Martin Segatz et al., Hydro's cell technology path towards specific energy consumption below 12 kWh/kg, *Light Metals* 2016, 301–305.
27. Philippe Julien and Jeffrey M Bergthorson, Enabling the metal fuel economy: green recycling of metal fuels, *Sustainable Energy & Fuels* 1 (3) (2017), 615–625.
28. Manuel Baumann et al., The Potential Role of Reactive Metals for a Clean Energy Transition, *Advanced Energy Materials* (2020), 2001002.
29. Proof of Concept, *Team SOLID,* https://teamsolid.org/proof-of-concept/ (accessed on 12.08.2022).
30. Giuseppe Antonio Elia et al., An Overview and Future Perspectives of Aluminum Batteries, *Adv. Mater.* 28 (35) (2016) 7564–7579.
31. Aluminium-Air: The Future of Electric Cars, *Aluminiumleader,* https://aluminiumleader.com/focus/aluminium_air_the_future_of_electric_cars/ (accessed on 12.08.2022).
32. MS Vlaskin et al., Computational and experimental investigation on thermodynamics of the reactor of aluminum oxidation in saturated wet steam, *International Journal of Hydrogen Energy* 35 (5) (2010), 1888–1894.
33. Wengang Bai et al., Comprehensive assessments of a novel aluminum-fueled energy storage system, *Energy Conversion and Management* 266 (2022), 115615.