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Conversion of Aluminum to Hydrogen: A Metallurgical Point of View

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Transition to the Net-Zero economy requires new sources of energy. Hydrogen is one of the promising candidates to replace carbohydrates. Emission-free technologies for hydrogen production are pivotal for this transition. However, the existing technologies to produce hydrogen are either polluting or energy-intensive. In recent years, a reaction of aluminum with water generating hydrogen has attracted a lot of attention. Most of the research is done with solid aluminum and analyzed mostly from the chemical and energy points of view. In this overview paper, rarely mentioned metallurgical aspects of this reaction are considered, as well as potential integration of the related technology into a green aluminum production cycle. The advantages of using liquid aluminum as well as related safety aspects are highlighted.

1. Introduction

Hydrogen is considered one of the pillars of future green energy-based economy and a cornerstone of the Net-Zero agenda. Therefore, its production in a manner that does not involve emissions is pivotal for the future application. Sadly, despite hydrogen being a clean fuel, most of its current production relies on technologies that are far from being eco-friendly being mainly dependent on “reforming” methane or other fossil fuels, leading to significant amount of CO_2 emissions. So, one can observe a full color spectrum of hydrogen, ranging from “brown” and “grey” to “blue” or “green,” depending on the production method.[1] Hydrogen made through water electrolysis is often referred to as green, but that is only true if the electricity used is sourced from 100% renewable sources, e.g., wind, hydro, or solar; which is often not the case. Also, water electrolysis is so energy-consuming that the question often arises whether it is more efficient to use the green electricity directly rather than for the electricity–electrolysis–hydrogen–energy route.

As an alternative, the conversion of solid aluminum to energy (heat and hydrogen) attracts more and more attention with the major investment in the US ($7B)[2] and a large EU project, Reveal,[3] running currently. In this conversion, the emission-free spontaneous reaction of water with aluminum is used to produce heat, hydrogen, and alumina (note that below 480 °C, aluminum hydroxide is produced instead of alumina[4]):

$$2\mathrm{Al} + 3\mathrm{H_2O} = \mathrm{Al_2O_3} + 3\mathrm{H_2} \tag{1}$$

As a result of this exothermic reaction, 1 kg of Al (solid) releases 15.1 MJ of heat (corresponding to $4.2\,\mathrm{kWh\,kg^{-1}}$ Al that can be converted back to electricity using a heat engine), 0.11 kg of H_2 (corresponding to about $4.4\,\mathrm{kWh\,kg^{-1}}$ Al), and 1.9 kg of alumina (Al_2O_3).[5]

A comprehensive review of advantages and disadvantages of using solid aluminum for producing hydrogen can be found elsewhere.[6]

It has been shown that the overall energy stored in aluminum can be converted to energy with the maximum 71% electric efficiency or 36.3% round trip efficiency, which is better than most liquid fuels (such as liquified natural gas, gasoline) and on par with methanol/dimethyl ether.[7] It does not matter much for the energy balance of the reaction if the solid or liquid metal is used, though the use of liquid aluminum is somewhat beneficial because the energy stored in the liquid metal is larger than in the solid ($9.4\,\mathrm{kWh\,kg^{-1}}$ Al liquid vs $8.6\,\mathrm{kWh\,kg^{-1}}$ Al solid[7]), as it includes the latent heat of fusion. As a result, the heat is released by the exothermic reaction, the hydrogen is emission-free, i.e., “green,” and the alumina (in the case of aluminum hydroxide, after additional processing) can go back to the electrolysis process to be converted back to aluminum.

2. Energy and Cost Analysis: Case for Using Liquid Aluminum in a Molten Aluminum Cycle

Main current interest in the process described by Equation (1) lies in producing “green” hydrogen and in using aluminum as a sort of “energy storage.” The primary production of aluminum is very energy consuming and part of this energy is “stored” in the metal with a possibility to get it back in a form of heat and hydrogen. This energy can then be used where it is needed and when it is needed. The argument is also that the resultant alumina can be returned to the Al production and converted back to aluminum, which will save some costs, energy, and reduce

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emissions in the bauxite processing (8 kWh kg^{-1} Al[4]), but will still require large energy to be spent on the electrolysis: alumina to Al (liquid) consumes (depending on the process) 11.5–16.5 kWh kg^{-1} Al with 50%–65% efficiency.[4,5] As one can see, the conversion of alumina into aluminum consumes more energy than one can get from conversion of aluminum to energy, which does not stop the increasing efforts to use the latter process for making "green" energy as it responds to the challenges of Net-Zero economy, providing an emission-free process.

Let us face the reality, also from the viewpoint of cost, the conversion of primary aluminum into hydrogen is not very efficient. With the current prices (based on LME data), the transformation of 1 kg of Al ($2.37) to 0.11 kg of H_2 ($5–6 kg^{-1} = $0.66 max) and 1.9 kg of Al_2O_3 ($0.34 kg^{-1} = $1.23) gives you a loss of $1.89–2.37 = −$0.48 kg^{-1}. Only when the scrap aluminum is used (current cost $1.58 kg^{-1}), there is some profit. There might be further a reduction in the aluminum costs when the recycled alumina is used for its production, around 43–60%,[5] but this is subject to the process used and expenses required to actually make this recycled alumina usable. Note that the product of a most conventional Al-to-H_2 conversion process (aluminum granules treated with water solution of sodium hydroxide at room temperature) is aluminum hydroxide contaminated with Na,[8] not pure alumina, which would require additional processing stages (calcination and purification) before electrolysis, consuming at least 0.83 kWh kg^{-1} Al_2O_3 or 1.6 kWh kg^{-1} Al.[4] On the other hand, the prices are volatile and the price of aluminum tends to go up while the price of hydrogen is down. In such a situation, the economic benefits of using even the recycled aluminum become marginal. Moreover, as the recycled aluminum (mostly alloy scrap) contains multiple impurities that will contaminate alumina, additional processing stages will be required at an energy and economical cost. In addition, there are inevitable energy and material losses in the process, so it is impossible to achieve 100% circularity and efficiency. Therefore, the importance of using aluminum in production of energy (heat and hydrogen) is not in the price or energy advantage but in the other benefits that respond to the environmental and, hence, societal needs.

It is important that the components of the technology, i.e., water and aluminum, are the most abundant and most recyclable chemicals on the planet; so there is a good chance that in some future, these two chemicals will form a basis for hydrogen-based economy.

There is no principal (energy or cost) difference between using aluminum for energy storage or energy (hydrogen and heat) production, it is merely a terminology used. The same goes for using liquid or solid aluminum. Solid aluminum has an advantage of easier transportation over liquid aluminum, but has disadvantages of losing 8.5% of the stored energy when solidifying as well as the need for energy/cost spent on transportation, milling (large surface energy needed for the reaction of solid Al with water), chemical additions (with the large surface energy, breaking the surface oxide layer is difficult and usually requires chemical like NaOH[8]), and purifying the resultant alumina or most likely aluminum hydroxide from the alkali and other contaminants. On the other hand, using liquid aluminium implies that we have liquid aluminium in hand, rather than melting solid aluminium, which would be very energy-consuming due to the large heat capacity of aluminium. Therefore, the use of liquid aluminum for energy production has a niche application in liquid metal operations, e.g., primary aluminum production, remelting in foundries and cast houses, and in recycling operations, where the liquid metal is present anyway. **Table 1** gives a summary of comparing these two routes.

The conventional aluminum production (Hall-Heroult process) by itself is both energy consuming and emits a lot of CO_2 due to the use of carbon anodes; hence, the produced aluminum is not "green." One component of reducing the emissions is the electrolysis process proper. A cleaner manufacturing technology using inert anodes has been investigated in recent decades. In this technology, the electrolysis using inert anodes produces aluminum and oxygen, effectively eliminating pollution.[5] Additional benefits include elimination of carbon electrode production, better thermal efficiency, and a reduced anode–cathode distance in the case of a wettable anode, which can improve the energy efficiency of the electrolysis cell.[9,10] The technology is currently in its pilot stage with ELYSIS (Alcoa/Rio Tinto) and Rusal, approaching the industrial scale in the next 5–10 years. Another part of making aluminum "green" comes from the electricity used. About 60% of energy associated with the primary production of aluminum comes from electricity spent.[9] Inert anode technology requires somewhat more energy than Hall–Heroult process,[10] which (in order to maintain environmental cleanliness) needs to be sourced in a "green" way, i.e., solar, hydro, geothermal, or hydrogen. At the moment there are already countries where more than 90% of electricity is produced using green sources (hydro, solar, and geothermal). To name a few: Iceland, Norway, Paraguay, DR Congo, Costa Rica, Uruguay, Kenya, Tajikistan, and Scotland.[11] Some of these countries, e.g., Norway and Iceland, are also major aluminum producers. The use of clean energy is, therefore, an essential component of reducing the CO_2 footprint of primary aluminum production. Hydrogen is a source of green energy that can be produced from the green aluminum itself. One can argue that there is no sense in converting relatively expensive aluminum into relatively cheap hydrogen, instead of selling it at a premium price. This narrative does not consider the environmental benefits, as the aluminum here is used as a source of "green" hydrogen with recycling the alumina back into production of "green" aluminum, contributing to the Net-Zero agenda and circular economy. To reduce the inevitable costs and energy, and improve the efficiency of this environment-friendly process, hydrogen needs to be produced as close as possible to the point of consumption. As a senior officer of Rio-Tinto stated: it is important "only produce hydrogen where we consume it" and that he "does not see green hydrogen as an energy carrier but does see a case for using it ....in alumina refineries".[12] It is important to recall that transportation of hydrogen from the point of production to the point of consumption requires its liquification, special precautions in transport, and then re-gasification. There might be some uses of aluminum for making hydrogen where the transportation of the solid aluminum would be necessary; but for incorporating this "green" energy source into the "green" aluminum processing cycle, there is no need for decoupling it from the aluminum processing proper. There is usually an argument that the use of aluminum as an

Table 1. Comparison of hydrogen production approaches using solid or liquid aluminum.

	Solid Al reaction	Liquid Al reaction
Stored energy	8.6 kWh kg^{-1} Al	9.4 kWh kg^{-1} Al
Requirements to starting materials	Large surface areas of solid aluminum particles (requires making powder or chips). Water temperature needs to be above 80 °C.	Liquid aluminum and water steam (temperatures above 600 °C).
Activation	Additions to break the oxide layer (alkaline or acidic solutions)	Not required (oxide layer can be removed from the surface mechanically)
Reaction location	Surface of the solid aluminum.	Surface and the upper layer of liquid aluminum with subsequent hydrogen dissolution and extraction from liquid metal.
Reaction product	Aluminum hydroxide (needs to be calcinated to make alumina suitable for electrolysis)	Alumina (can be returned directly to electrolysis)
Safety	Requires pressurized vessels, caution about aggressive/corrosive agents used.	Introduction of water steam inside the volume or underneath should be prevented.
Location of use	Typically separate from the aluminum production locations.	Preferably the location where liquid aluminum is present (smelter, recycling, or casting plant).
Advantages	Relatively straightforward technology.	Higher stored energy.
		Reduced need for activation agents.
	Can be used in any location where needed.	Produced alumina can be used in electrolysis.
	Low temperature.	Can be incorporated in molten aluminum processing cycle.
		Flexibility in the fraction of liquid metal that is converted, with the rest going to the downstream processing being already degassed.
Disadvantages	Less stored energy.	High temperatures are only viable if the liquid aluminum is present (hence, molten metal operations).
	Requirement for activation (corrosive agents to disrupt oxide layer).	Safety issues that need proper handling of molten aluminum (keeping up with industry standards).
	Safety issues related to the use of corrosive agents.	Needs additional processing step of extracting dissolved hydrogen.
	Costs and energy associated with purchase, transport, and milling of solid aluminum.	
	Produced aluminum hydroxide needs additional processing.	
	All aluminum needs to be converted.	

energy storage allows it to be used only when it is necessary, e.g., during dark winter months when solar energy supply is scarce.[4] This is a true argument if we use this energy for heating houses or lighting streets, but if we use this energy in the metallurgical cycle, it is inefficient to decouple it from this cycle.

Following the narrative of "energy storage" that can compensate for the energy lost due to the seasonal oscillation in the supply (e.g., solar), this technology can be used in the liquid metal operations when it is necessary to compensate for the lack of other "green" energy sources, with the "green" heat and hydrogen produced by the reaction of liquid Al with water steam. The same goes for the recycling operations where the melting of scrap is involved. The only difference is that we use aluminum as an energy storage for a short period of time while the metal is still liquid and return back some of the stored energy to the liquid metal processing (electrolysis of alumina, melting of recycled scrap, or other operations) in a form of heat and hydrogen with an added value of returning alumina to the electrolysis (or selling it). In addition, there is a greater thermodynamic stimulus for the reaction initiation at higher temperatures (molten metal). Some of the heat produced as a result of the reaction can be used for maintaining the metal in the liquid form. There is another advantage of using the liquid Al over using the solid one as the issues with the surface oxidation can be dealt with in a much easier way without adding corrosive chemicals or alkali metals that will contaminate the alumina. It is also important that in this process, there is no need to transform all aluminum into energy, only the necessary fraction is converted, with the rest going to downstream operations and eventually to consumers.

3. Metallurgical Analysis of Technological Approaches

As we already mentioned, there are two technological routes for the reaction (1) to be utilized for hydrogen production, one is using solid aluminum and the other is using liquid aluminum (melt). The first route is extensively studied and being commercialized now[2,3] as it is relatively simple, i.e., solid aluminum (primary or recycled) is milled to granules or powder and subjected to the reaction with water mixed with some chemicals (typically alkali-containing) to activate the reaction and disrupt the solid oxide skin on the aluminum surface.[8] If the reaction occurs at room or slightly elevated temperatures, the only gaseous phase is hydrogen, so it can be easily separated and extracted. If water steam is used, the separation of incoming steam and outcoming hydrogen poses a very difficult problem, so this route is seldom practically used. As we already mentioned, this route has advantage of allowing aluminum to be transported and used in the location where the energy is needed but at the expense of losing some of the stored energy upon solidification, spending energy and money on transportation, milling, recovering of alumina from aluminum hydroxide, and purifying alumina from contaminating alkali impurities. The second route is reported in some papers[13] and patents[14–16] but seldom implemented due to the reasons outlined below.

To the best of our knowledge, the engineering of using liquid aluminum for hydrogen production was done without any regard to the metallurgy. If we exclude patent[14] that somehow suggests that the water steam coming on the top of the melt can be separated from hydrogen coming from the top of the melt (which is unlikely), all other solutions incorporate barbotage of water or water steam through the aluminum melt with the reaction happening inside (!) the melt on the surface of the vapor bubbles and the generated hydrogen bubbling up to the surface while the formed alumina settling to the bottom of the melt. As patent[16] says and this is representative of other proposals in literature: "the arrangement allows injection of a reactant gas into the gas space of the generator, from which it bubbles through the liquid reactant. As it bubbles through the liquid reactant, the desired gas generating chemical reaction occurs, and the product gas collects in a separate gas space from whence it is withdrawn." "During this bubble stage, any unreacted gas reacts with the liquid fuel and the product gas is generated, which continues rising through the liquid fuel until it reaches the discharge gas space." "…Solid product, e.g., an oxide…generally has a sufficiently higher specific gravity that that of the liquid fuel that they will settle by gravity to the lower part of the vessel." In these quotes, "liquid fuel" is molten aluminum, "reactant gas" is water steam, and the "desired gas" is hydrogen. These suggestions contradict the metallurgical understanding of the reaction of water and hydrogen with liquid aluminium, and inherently present grave safety hazards.

As we know, the reaction between liquid aluminum and water is exothermal and the oxidation of aluminum releases a lot of energy: 1 kg of aluminum reacting with oxygen from water vapor is equivalent to detonating 3 kg of trinitrotoluene (TNT).[17] Of course, we do not want this explosion to happen inside the bulk melt where there are no paths to dissipate the generated energy. That is why it should never be allowed for this reaction to happen inside the bulk of liquid aluminum, as it may result and have resulted (in cast houses and foundries) in serious explosions, injuring personnel and damaging equipment. The other reason why the suggested schemes cannot work is based on the unique interaction of hydrogen with liquid aluminum, which the inventors were obviously unaware of. Hydrogen, unlike other gases, has a very high solubility in liquid aluminum, which is increased with the water vapor pressure.[18,19] As a result of large partial pressure of H_2 at the interface between water steam and liquid Al, the potential amount of dissolved H_2 in liquid Al at 727 °C and atmospheric pressure conditions can be as high as 0.3×10^6 $cm^3/100$ g or 27 g $H_2/100$ g Al. Although these values are not practically achieved due to the barrier oxide layer and dynamic equilibrium at the interface, values from 4 (pure Al) to 44.5 (Al-5% Zr alloy) $cm^3/100$ g were reported.[19]

Therefore, hydrogen produced by the reaction of liquid aluminum with water steam will dissolve in liquid aluminum and not bubble out as is alleged in some patents. To force hydrogen out of the liquid solution, special techniques known as degassing need to be implemented (none of those is even mentioned in the papers and patents on hydrogen production). These techniques may involve vacuum, cavitation, or purging with inert gas.[19,20] After degassing, the amount of hydrogen in liquid aluminum can be dropped to the levels below 0.1 $cm^3/100$ g with the rest used in energy production. Alumina formed as a result of such a reaction will not settle to the bottom of the vessel but will either stay on the surface or float to the surface due to hydrogen adsorbed to its surface (part of supersaturated hydrogen will precipitate on the available interfaces). As a result, the surface of the melt will be quickly covered with dross, which will prevent free hydrogen evolution to the surface, even if this becomes possible (see the arguments above).

Due to these metallurgical reasons, there are almost no practical implementations of this approach. In ref. [13] where an attempt was made to "bubble" steam through the aluminum melt, our conclusions were confirmed. It was stated that "It was unexpected (?) that the hard reaction products (basically, alumina) were collected not in the reactor bottom but in the surface melt layer, floated a porous crust." "The thick foam layer of same reaction product was formed when the reaction occurred at intensive barbotage regime." It was also confirmed that "bubbling" regime is not working for hydrogen generation: "The principal limitation on the hydrogen generation efficiency for higher steam flow rates is caused by development of the barbotage instability such as a coalescence of steam bubbles and occurrence of the steam breakthrough through the melt."

Therefore, the reaction of liquid aluminum with water vapor should be implemented based on the metallurgical knowledge and safety and include at least three stages, i.e., reaction at the melt surface, dissolution of hydrogen in the melt, and extraction of hydrogen from the melt using noncontaminating methods, e.g., ultrasonic cavitation or vacuum. Such a technology can be part of the liquid metal operations, providing additional sources of green energy, e.g., in aluminum refineries. This concept and technology are now being patented.[21]

4. Conclusions

1) The hydrogen production using the reaction of aluminum with water is important from the viewpoint of Net-Zero challenges as it is emission-free, but should not be considered as highly economically or financially beneficial as compared to more conventional yet "dirty" technologies. The benefits lie in environmental and societal benefits. Moreover, as aluminum and water are abundant on Earth, this way of hydrogen production may become the mainstream in the future energy harvesting. 2) The hydrogen production using the reaction of liquid aluminum with water vapor has benefits over using solid aluminum and water solutions as follows: larger energy stored in liquid aluminum; higher rate of reaction; relative simplicity in removing the reaction products; and alumina as the by-product that can

be returned directly to the electrolysis cycle. 3) Metallurgy of water and hydrogen reaction with liquid aluminum needs to be taken into account when developing a technology to assure safety and feasibility of the process. 4) The dissolution of hydrogen in the molten aluminum and its extraction are the necessary stages that provide safety and plausibility of the technology.

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Conflict of Interest

The author declares no conflict of interest.

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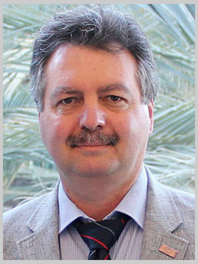

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