Hydrogen Generation by Treatment of Aluminium Metal with Aqueous Solutions: Procedures and Uses

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Additional information is available at the end of the chapter

1. Introduction

The use of energy on a large scale has been a determining aspect of the world economy in modern times. For the last several centuries, this energy has come mainly from the transformation of combustible fossils, in the form of peat, coal, petroleum, and natural gas. During the year 2003 the supply of primary energy ran to 10,579 Mtoe (443 EJ), and this number represented a 75% increase over 30 years [1]. Of this, 80% came from fossil fuels. In 2003, the production of electricity worldwide was still dominated by coal (40%), followed by natural gas (19%), and nuclear and hydro generation (15% each) [1].

In contrast to the overall energy requirements stated above, transportation depends almost exclusively (to 95%) on petroleum and its derivatives; the problems surrounding this resource will necessitate the investment of an estimated 16 trillion U.S. dollars to develop and update new ways to power vehicles [1]. Bauen [1] mentioned that, in order to reduce CO_2 emissions, in the future we could use a pre-combustion at the coal plants, producing 250 Mt of hydrogen per year, which is six times the present production. He held out a vision of use of fuel cells for the transformation of energy and its use in hybrid vehicles which would use as their fuel hydrogen produced from water. With respect to the energy invested during a process, Liu et al. [2] state that apart from a qualitative understanding of the energy, a quantitative understanding is essential, analyzing an industrial process in terms of the material flow and amount of energy, using as example an analysis of the statistical data from an aluminum refinery at Zhenzhou, China.

Research on renewable energy sources is, in large measure, driven by the expectation of future shortages in the supply of crude oil. In the U.S.A., maximal crude-oil production

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occurred in the 1990s [3]; this event was termed "Peak Oil" for the American case. Other important oil producers, such as Mexico, Indonesia, United Kingdom, Norway, Romania, are also clearly beyond their date of maximal production. As to the timing of Peak Oil on the worldwide scale, different workers have, at different times, made their predictions; some of these are summarized in Table 1. Most of these forecast that Peak Oil was less than a dozen years away from the date of their prediction, though some predictions are slightly more sanguine [15], [17]. But even if, by dint of new exploration, new crude-oil production technologies, more efficient use of this resource, and the development of alternative energy technologies the actual Peak Oil date has continually been deferred, this signal event will probably take place at some point in the relatively near future. This represents a substantial menace for the world economy, in light of the increasing energy demand of major, rapidly industrializing national economies, especially in Asia and South America.

Date of forecast	Peak Oil date	Reference
2000	2004-2014	Bartlett [4]
2001	Beyond 2020	Deffeyes [5]
2002	2011-2016	Smith [6]
2003	Around 2010	Campbell [7]
2004	2006-2007	Bakhtiari [8]
2005	After 2010	Koppelaar [9]
2006	After 2010	Skrebowski [10]
2007	2008-2018	Robelius [11]
2008	2035	CERA, [12]
2008	2010-2011	Hirsch [13]
2009	2015	de Almeida [14]
2010	2030	Aleklett [15]
2011	2015-2020	Murphy [16]
2011	2035	Winch [17]

Table 1. Peak Oil dates projected by various authors.

The wide use of crude oil, and of fossil fuels in general, has also given rise to a separate, but equally pressing concern: that the liberation of carbon dioxide to the atmosphere attendant on the use of these fuels is having a major, and potentially accelerating, deleterious climate effect, which may impinge in critical ways on the world economy and the well-being of mankind. The two considerations are independently important: even if easily accessible, vast new oilfields were to be found in the near future, relieving the supply concerns in this area, the continuous increase in atmospheric CO_2 over the past decades is deemed to be of sufficient concern to warrant worldwide, concerted efforts to reduce production of this gas, mainly by switching energy production on a large scale to new, alternative forms, which minimize or entirely avoid the formation of this by-product.

2. Overview

2.1. Hydrogen production

A promising part in the new developments of energy technologies is played by hydrogen. It is not a primary fuel, as no hydrogen can be mined on our planet; rather it has to be considered an energy vector, a material produced by an endergonic chemical process starting from hydrogen-containing compounds, and whose chemical potential can in turn be converted to other forms of energy, by combustion in air, through fuel cells, or by other means. Hydrogen is, thus, useful as a storage form of energy derived from intermittent sources such as wind power, to later be transformed to electricity when and where required. An important application would be as a portable energy source in automotive transport, where hydrogen fuel cells now operate with an efficiency of about 40%, and perhaps 50% in the near future, while gasoline- or diesel-operated internal-combustion engines have efficiencies of 25%-30% under real driving conditions [18]. Also, fuel-cell powered vehicles are mechanically simpler, facilitating new designs in automobile construction. Finally, and importantly, fuel cells with proton membranes only release water to the environment, an innocuous product.

On our planet, hydrogen occurs naturally in the form of compounds such as water or hydrocarbons. It can be produced in elementary form through partial combustion of fossil fuels, as in reforming of natural gas, in coal gasification, through high-temperature electrolysis, e.g. at operating temperatures of 800°C in nuclear reactors [19], or from renewable energy by processes such as water electrolysis, water photoelectrolysis, or biomass gasification. In 2007 about 50 million metric tonnes of hydrogen were used worldwide, mainly in the production of ammonia fertilizers, in chemical syntheses, and in refining processes [20]. 95% of the hydrogen production is in a captive mode (i.e. it is produced where it is used) starting from fossil fuels (50% from natural gas, 30% from crude oil, and 20% from coal). However, from an economic-environmental point of view, the most favourable method of hydrogen production is starting from renewable energies, mainly from hydro and wind energies through electrolysis; nonetheless, water electrolysis only accounts for 4% of total worldwide hydrogen production [21], even though as far back as 1977 there was already an international consensus about the need for a concerted initiative to develop water-electrolysis technologies such as aqueous water electrolysis, solid-polymer and solid-oxide water electrolysis, and electrocatalysis [22].

Another method of hydrogen production is the reduction of water using aluminium or its alloys. Because of its light weight and great strength, aluminium is widely used for structural purposes, but it also offers important advantages for its potentially wide employment as an energy carrier: its high energy density, of 29 MJ/kg, the fact that it is the most abundant metal in the earth´s crust, and its highly negative standard redox potential (ε_0 = -1.66 V) which makes it, in principle, an excellent reducing agent, capable of producing hydrogen gas upon contact with water, in a corrosion process which does not entail production of CO_2. This type of reaction can be carried out with the help of alkali, or under neutral conditions, or at elevated temperatures, or via reaction of aluminium with alcohol [23]. As a practical example for the high energy density of aluminium, it can be calculated

that an electrical automobile energized by fuel cells could run a distance of 400 km with about 4 kg of hydrogen which could be obtained from 36 kg of aluminium via an aluminium-water reaction [23]. This example points out the advantages inherent in the use of aluminium metal as a compact source of hydrogen; by contrast, storage of hydrogen at standard temperature and pressure requires volumes 3000-fold larger than for gasoline, and in liquid state it is necessary to take it to temperatures of -253°C through cooling systems, which entails additional important energy costs.

The aluminium-water reaction produces energy in different forms, all of which are potentially usable: heat, water vapour, and hydrogen gas. The water vapour and hydrogen gas formed can be used to power a turbine, and the hydrogen gas furthermore represents an energy reservoir to be used by high-temperature combustion or to feed fuel cells. Such systems have been quantitatively modeled [24], [25] and [26].

2.2. Aluminium production

The main prime material for aluminium production is alumina (Al_2O_3), found in a large number of natural minerals. 98% of metallurgical alumina is produced by the Bayer process [27] starting from bauxite, a mineral composed to 50%-80% of hydrous alumina (aluminium hydroxides and oxyhydroxides). A simplified rendition of the chemistry underlying the Bayer process is given in the equation:

$$Al_2O_3 \bullet nH_2O + 2NaOH \rightarrow 2NaAlO_2 + (n+1)H_2O \qquad (1)$$
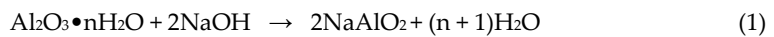
The production of 1 kg of aluminium takes about 2 kg of alumina, which would be derived from 4 kg of bauxite. The energy investment in 1 kg of aluminium is 29.6 MJ for the obtention of the prime material (i.e. bauxite mining, alumina refining, and production of the carbon anodes) and 56 MJ for the electric work of alumina reduction. As the heat content required by the carbon for each kg of aluminium is about 14 MJ, the total energy investment of the aluminium is about 100 MJ/kg [28].

As stated before, it is of advantage to produce the hydrogen at the point of use, therefore, portable systems are required, based on electrochemical oxidation of the aluminium [29], or on the aluminium-water reaction in alkaline conditions, or on the oxidation of mechanochemically or mechanically activated aluminium [29]. Theoretically the electrochemical oxidation has an energy density of 4300 Wh/kg and an electrical efficiency of 55%. Chemical-oxidation technologies with aluminium can reach energy densities of 1040 Wh/kg and electrical efficiencies of 25%. As a reference in the comparison of efficiencies Schwarz et al. [30] stated that power plants which use heat derived from fossil fuels have efficiencies of 53% in the case of natural gas, 48% for crude oil, and 43% for coal.

3. Performance of the aluminium-water reaction

Because of its low equivalent weight, aluminium is an excellent potential producer of hydrogen by weight, though it is outdone in this regard by sodium borohydride, which in

hydrolysis can produce 2.4 litres of hydrogen gas per gramme of substance. Aluminium and magnesium have values of 1.245 L and 0.95 L per gramme respectively, while their corresponding hydrides, AlH_3 and MgH_2, produce 2.24 L g^{-1} and 1.88 L g^{-1}, respectively [31].

Due to its highly negative redox potential, aluminium should react easily with water, producing hydrogen gas and $Al(OH)_3$ according to the equation:

$$2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3 \tag{2}$$

In practice however, aluminium is generally passivated by formation of a tightly adhering surface film. For example, when exposed to air, the surface of aluminium metal is rapidly oxidized to form a tight layer of aluminium oxide, which prevents further penetration of oxygen, thus protecting the underlying metal from further oxidation. This passivation of the aluminium also interferes with the aluminium-water reaction at the interface between metal and liquid. Surface oxidation of the aluminium also comes about as a result of the aluminium-water reaction itself, and may also constitute a limitation to the rate and yield of the reaction. Overcoming these impediments is a central problem in all practical applications of the aluminium-water reaction.

The passivating surface layer of Al_2O_3 is an amphoteric material, soluble in both strongly acidic and strongly basic aqueous solution. Therefore, both acidic and basic hydrolysis of aluminium can be employed for hydrogen production. However, the corrosive character of the solutions employed in these instances is of disadvantage in practical applications. Accordingly, a large part of the recent research in this area has centred on methods to promote the aluminium-water reaction in neutral or near-neutral conditions, by employing special aluminium alloys, by addition of activators, by mechanical pretreatment of the aluminium, or by irradiation.

For several decades, aluminium alloys with gallium and indium have been studied as highly reactive materials in the aluminium-water reaction, as the minor-metal admixtures cause embrittlement of the metal and destruction of the intergranular bonds and of the passivating aluminium oxide film. The activation of aluminium powders by grinding or co-milling with gallams of various compositions, Ga-In (70:30), Ga-In-Zn (70:25:3), Ga-In-Sn (62:25:13), Ga-In-Sn-Zn (60:25:10:5), leads to significant rates of hydrogen gas evolution on water contact [31] [32]. These are in the range of 14-20 mL g^{-1} min^{-1} with powders prepared by soft mechanical treatments, but can be two orders of magnitude higher, at 1000 - 2500 mL g^{-1} min^{-1}, in the case of the milled powders. The rate of the reaction rises with increasing admixture of the gallam, up to 10 wt%, relative to the aluminium, and with the reaction temperature. The cost of the gallams is, obviously, a consideration; still, a 2%-3% admixture of gallam and a temperature of 60°C bring about hydrogen evolution rates of 2000 mL g^{-1} min^{-1}. Materials with lower gallium content, however, perform more poorly, and an increase in the concentration of cheaper dopants (Sn, Zn, Pb) is ineffective [33].

Certain aluminum-based composites, generally containing aluminium at 80 wt%, doped with gallium, indium, zinc, or tin, obtained by co-melting of the metallic components, have been studied by powder X-ray diffraction, differential thermal analysis, and EDX [33]. The

tests indicated the presence of a crystalline aluminium metal phase, an intermetallic compound, $InSn_4$, and a eutectic in the Ga-In-Sn-Zn system, melting at 6°C, distributed over the grain boundary space. Some of these alloys performed satisfactorily in the aluminium-water reaction, forming hydrogen and amorphous precipitates of the corresponding metal hydroxides; however, they lost effectiveness upon storage at room temperature, and were completely stable only in vacuum at liquid-nitrogen temperature.

Shaytura et al. [34] studied the aluminium-water reaction in the presence of an undisclosed chemical activator which interacts with the OH-groups of the $Al(OH)_3$ formed during the reaction, thereby affecting the pore size distribution in the newly made oxide layer, which facilitates permeation through this layer and thus the hydrogen-forming reaction. Similar effects of better pore-size distribution and faster hydrogen evolution were also obtained by applying an ultrasonic field to the reacting mixture.

Czech and Troczynski [35] found that the passivation of aluminium metal in water in the pH range from 5 to 9 is significantly suppressed when the metal has been milled with inorganic salts, such as KCl o NaCl. Corrosion of this type of aluminium in tap water, with production of hydrogen and precipitation of aluminium hydroxide, at normal pressure and a temperature of about 55°C, is rapid and substantial. By way of example, 92% of the aluminium in the Al-KCl system (milled for 1 h) is corroded in 1 h, in aqueous solution at neutral or near-neutral pH, with liberation of 1.5 mol of hydrogen for each mole of aluminium consumed in the reaction. Apart from gaseous hydrogen, only solid aluminium hydroxides are formed as by-products of the reaction; this is a promising aspect for direct recycling from this system.

Similarly, Alinejad and Mahmoodi [36] proposed a simple method for hydrogen generation, based on highly activated aluminium and water. Activation was achieved by milling aluminium powder with sodium chloride as a nano-miller. The mean rate of hydrogen release per gram of aluminium was 75 ml/min, for powder prepared with a salt/aluminium molar ratio of 1.5, and 100% yield was reached after 40 minutes.

Mahmoodi and Alinejad [37] also reported preparing highly active material for the aluminium-water reaction by ball-milling the metal with a large amount of sodium chloride as a nano-miller, in a dilute argon atmosphere. The powder obtained could be stored for a long time; once submerged in hot water, it was rapidly hydrolysed, and hydrogen was produced in a 100% yield. The rate of hydrogen generation was found to depend critically on the initial water temperature. The heat released in the exothermal aluminium-water reaction was employed to raise the water temperature during the reaction. The mean rate of hydrogen production was ~101 and ~210 ml/min per 1 g de Al, using initial water temperatures of 55°C y 70°C, respectively. However, distinctly higher rates of hydrogen evolution were achieved (713 mL g^{-1} min^{-1}) when the aluminium was activated by ball milling with 7 wt% bismuth.

Wang et al. [38] used nanocrystals of metal oxides such as TiO_2, Co_3O_4, Cr_2O_3, Fe_2O_3, Mn_2O_3, NiO, CuO, and ZnO as modifiers in aluminium metal powders to produce hydrogen by a

room-temperature reaction with deionised water or tap water. They studied the effect of TiO_2 nanocrystals of different crystal size on hydrogen production in the reaction with tap water, and showed that the water quality and the metal-oxide nanocrystals such as TiO_2, Co_3O_4, and Cr_2O_3 increase hydrogen production by the reaction of the aluminium powder in neutral water at ambient temperature.

Mercury or zinc amalgam have been used as activators to promote the hydrolysis of aluminium [39]. The results showed that in the presence of mercury or zinc amalgam aluminium hydrolysis to generate hydrogen could take place at room temperature, in distilled water. The rate of hydrogen release depended on the reaction temperature, and the maximum rate of hydrogen generation was 43.5 cm^3 h^{-1} cm^{-2}, obtained at 65°C with the zinc-amalgam technique. For this method, the apparent energy of activation for aluminium hydrolysis induced by zinc amalgam had a value 43.4 kJ mol^{-1}, while in the case of the mercury method it was 74.8 kJ mol^{-1}. The results of the X-ray diffraction analysis showed that the subproduct formed is bayerite.

Deng et al. [40] used three different modification agents, γ-Al_2O_3, α-Al_2O_3, and TiO_2, to surface-modify aluminium particles. The selected oxide was ball-milled with the aluminium metal in ethanol suspension, using highly pure Al_2O_3 spheres. They investigated the effect of different modification agents on hydrogen generation in the reaction of aluminium powder with water. The different modification agents were seen to have different effects on the dynamics of the aluminium-water reaction. In particular, induction times for the reaction increased in the series: γ-Al_2O_3-modified aluminium < α-Al_2O_3-modified < TiO_2-modified, interpreted as the series of increasing energy barriers for nucleation of hydrogen bubbles on the variously modified metal surfaces.

Fan et al. [41] prepared a series of aluminium-based materials by ball-milling and/or fusion; they used the techniques of XRD, SEM, and TG-DTA to characterise the samples. They evaluated the effects of different alloying metals, such as Zn, Ca, Ga, Bi, Mg, In, and Sn, on hydrogen generation through hydrolysis in pure water. They found mechanical milling to be preferable to melting as a method to produce aluminium alloys containing metals with low melting points (Ga, In). The addition of Sn, Ga, or In could reduce the hydrolysis rate of the Al-Bi alloy, but the addition of Zn accelerated the hydrolysis of this alloy. Best yields of hydrogen were obtained with quinternary alloys containing Al, Bi, Zn, Ga, and calcium hydride.

Parker et al. [42] developed a process to obtain hydrogen by the reaction of mixtures of finely divided magnesium and finely divided aluminium with seawater, at normal pressure and temperature. The procedure is appropriate for fixed applications where no electric net is available, it requires no or only a minimal supply of electricity. As a side product a mixture of magnesium hydroxide and aluminum hydroxide are obtained; these side products have a high market value as prime materials for the production of thermal and electrical insulation (i.e. heatproof sheathings or linings).

Soler et al. [43] experimented with aluminium strips in aqueous solutions of NaOH or KOH, at alkali concentrations of 1 to 5 M and temperatures between 290 K and 350 K, and found a

maximum hydrogen production per gramme of aluminium of 3100 cm^3 min^{-1} with 5 M NaOH at 350 K, while the use of 5 M KOH at 350 K gave a rate of 2900 cm^3min^{-1} per gramme of aluminium.

Macanás et al. [44] examined the effect of the presence of various inorganic salts, at a concentration of 0.01 M, as corrosion promoters in the reaction of metallic aluminium in 0.1 M NaOH at 75°C and found the advantages of 100% yield of hydrogen production, self-initiation without heating, and significant accelerating effects (almost two-fold in the case of NaF, and 1.5-fold with $MgCl_2$, $Fe_2(SO_4)_3$, Na_2SO_4, and $FeCl_3$). High rates and good yields of hydrogen were also achieved in the absence of NaOH with the use of mixed solutions of sodium aluminate, sodium stannate, and sodium metaborate, each in concentrations between 0.1 M and 0.5 M. In almost all of these experiments, beginning and end values of pH were between 12 and 13.

The use of solutions containing only sodium aluminate was examined by Soler et al. [45] in comparison with NaOH solutions giving the same initial pH value; similar results both in terms of yields and of maximum hydrogen flow rates were obtained, leaving in doubt whether there is a specific chemical effect of the aluminate, especially as this salt was used in high concentration (0.5 M). For the sodium aluminate case, an Arrhenius energy of activation of 71 kJ mol^{-1} was determined, interpreted as indicating that the rate-controlling step in the process was a chemical event.

The aluminium-water reaction in the presence of sodium stannate at 0.075 M (Soler et al., [46]) gives interesting results in terms of acceleration. In this case, the reaction is affected from its earliest stages by formation of metallic tin as a by-product, noticeably reducing the hydrogen yield and complicating the product mixture. The energy of activation of the hydrogen formation was determined at 73 kJ mol^{-1}.

Uehara et al. [47] observed that when aluminium metal was cut under water effervescence occurred at the freshly cut surface, which however soon subsided. The method is obviously not applicable as a practical way to produce hydrogen gas; nonetheless, the observation serves to illustrate the problem of rapid passivation under water and the need to address this issue in a realistic manner to produce hydrogen in the aluminium-water reaction, e.g. through addition of appropriate activators.

Watanabe [48] studied the mechanism of the aluminium-water reaction in aluminium powders with particle sizes in the micron and sub-micron range, obtained by mechanical grinding, and came to the following conclusions. Micro-cracks formed at grain boundaries at the surface of the metal particles grow inward, due to corrosion by water. Inside these fissures, unsaturated aluminium atoms (with one free bond or two free bonds, i.e. (Al=) and (Al-)) may conform, with other such atoms, clusters which split the water molecules present in the crack, with initial formation of AlH_3, and hydroxylated aluminum species in the crevice wall. The formation of these species creates internal stresses in the metal, extending the micro-cracks, by a kind of micro-tribochemical effect. The AlH_3 further reacts with water, producing diatomic hydrogen.

In a simulation using the reactive force-field method (ReaxFF), Russo et al. [49] examined the dynamics of water dissociation at the surface of aluminium nanoclusters, over time periods of up to 70 ps, and with different numbers of total participating water molecules. Interestingly, an optimum water concentration (of about 30 water molecules per Al_{100} cluster) was found, indicative of two countervailing effects: the need for some additional solvating water molecules to assist the reaction of the aluminium-adsorbed water undergoing reaction, and surface saturation of the aluminium surface at high water concentration, sterically hindering the binding of hydrogen to the cluster.

Table 2 summarises further results reported with different mixtures as prime materials for the aluminium-water reaction. A few examples of the related magnesium-water reaction are also included.

Mixture	Process	Rate of hydrogen production	Source
Hydrogenated Mg_3La + water	Hydrolysis, during the first 20 minutes	43.8 ml min^{-1} g^{-1}	Ouyang et al. [50]
Hydrogenated La_2Mg + water		40.1 ml min^{-1} g^{-1}	
Milled Mg + sea water	Hydrolysis, during the first 10 min	90.6 ml min^{-1} g^{-1}	Zou et al. [51]
Milled Mg/Co (95:5) + sea water	Hydrolysis, during the first minute	575 ml min^{-1} g^{-1}	Zou et al. [51]
Milled Al/Bi/NaCl (80:15:5) + water	Hydrolysis, during the first 30 min	300 ml min^{-1} g^{-1}	Fan et al. [52]
Milled Al/Bi/CaH_2 (80:10:10) + water	Hydrolysis, during the first 3 min	340ml min^{-1} g^{-1}	
Milled Al/Bi (80:20) + water	Hydrolysis, during the first 30 min	24 ml min^{-1} g^{-1}	
Al-20%wt CaH_2	Hydrolysis, during the first 5 min	24 ml min^{-1} g^{-1}	
$Ni_{20}Al_{80}$ + 0.46 M NaOH	Hydrolysis, during the first 15 min	63 ml min^{-1} g^{-1}	Hu, et al. [53]
$Ni_{30}Al_{70}$ + 0.46 M NaOH	Hydrolysis, during the first 15 min	54 ml min^{-1} g^{-1}	
$Ni_{40}Al_{60}$ + 0.46 M NaOH	Hydrolysis, during the first 20 min	47 ml min^{-1} g^{-1}	
$Ni_{50}Al_{50}$ + 0.46 M NaOH	Hydrolysis, during the first 60 min	7.3 ml min^{-1} g^{-1}	

Table 2. Mixtures of water, aluminium, and other materials, for hydrogen production

4. Applications of the aluminium–water reaction

4.1. Thermal energy

A special type of application of the aluminium-water reaction, which emphasizes the thermal aspect, was described by Sabourin et al. [54], who carried out the combustion of nano-aluminium (38 nm diameter particle size) in mixtures of liquid water and hydrogen peroxide. They obtained, at 3.65 MPa argon pressure, mass burning rates per unit area between 6.93 g cm^{-2} s^{-1} (at 0% H_2O_2) and 37.04 g cm^{-2} s^{-1} (at 32% H_2O_2), corresponding to linear burning rates of 9.58 cm s^{-1} y 58.2 cm s^{-1}, respectively. The difficulty lies in the high cost of the preparation of aluminium on the nanoscale for its combustion [55].

There are various techniques to prepare aluminium on the nanoscale, such as the electro-exploded wire method cited by Kotov [56] and by Kwon et al. [57], explosion in plasma [58], plasma electro-condensation process [59], sol-gel [60], heating evaporation [61], and evaporation [62], for which two routes can be used: induction heating evaporation (IHE) and laser-induction complex heating evaporation (LCHE). For the "IHE" method one uses a chamber which contains an induction coil; in the centre of the coil are located two crucibles, one made of graphite, the other of alumina. The alumina crucible is charged with aluminium of 99.6% purity, while the interior of the chamber holds a dilute argon atmosphere at 10 Pa pressure. The coil is energized at high frequency at an initial power of 5 kW; after several minutes the aluminium metal has melted. The coil is deenergized, and the molten liquid rapidly evaporates; these atoms of evaporated aluminium are collected through collisions with the argon gas, producing in this manner aluminium nanopowders. For the "LCHE" method the equipment is fitted with a continuous-wave 1.6-kW CO_2 laser; this laser is switched on when the aluminium has molten and vaporises it rapidly, in the subsequent condensation step aluminium nanopowder is again obtained. The thermal properties were determined by Chen et al. [62] using thermogravimetric (TGA) techniques and differential thermo-analysis (DTA), finding that the temperature peaks were at 560°C and 565°C, and the enthalpy increases were 1.18 kJ/g and 3.54 kJ/g for "IHE" y "LCHE", respectively.

Shafirovich et al. [63] proposed the use of $NaBH_4$/metal/H_2O, were aluminium metal in powder form can be used, thus reducing the extra cost entailed in the preparation of nanoparticulate aluminium. In their experiments they used different stoichiometric ratios, with the result that the mixtures containing powdered aluminium do not burn as easily as when nanoscale aluminium is used. To resolve this problem they added magnesium in powder form as an activator, thus achieving combustion. Here again, the main result is the thermal effect, with only a minor yield of hydrogen.

A different type of thermal application with Al/H_2O/NaOH, where the aluminium used was the shavings from lathes and milling machines, i.e. aluminium pieces on the centimeter scale, was described by Olivares-Ramírez et al. [64]. In this system, in a first stage hydrolysers are used to obtain hydrogen through the chemical reaction between aluminium, sodium hydroxide, and water, the hydrogen obtained is then passed through water to trap

the vapour generated in the original exothermal reaction; finally the hydrogen is burned in air. The second stage consists of a refrigerator based on the ammonia-water absorption principle, energized by the heat produced in the combustion of the hydrogen.

4.2. Fuel cells

Hydrogen is the fuel most frequently used in fuel cells. At present, microfuel cells are being developed for applications in portable electronic devices, to address the problem of hydrogen storage in a portable mode. The difficulty lies in that we do not yet have portable systems for hydrogen storage; for instance, even a small hydrogen container, to energize a laptop computer, would not be allowed onto an airplane. Small aluminium-water reactors, however, could supply this need [65]. The hydrogen could be produced from variegated sources, such as electrical wire, metal hydride, or aluminium foil.

Jung et al. [66] describe a small-scale hydrogen generator, in which two types of additives, NaOH or CaO, are used to control the flow of the hydrogen generated, with the idea that this could be connected to a small fuel cell. In their experiment they feed the reactor, through a micro-pump, with NaOH solution at a rate of 0.2×10^{-6} $m^3 min^{-1}$, at a pressure of 1500 kgf cm^{-2}, and NaOH at concentrations of 5%, 10%, 15% y 20% (w/w), achieving a maximum hydrogen production of 2.65×10^{-3} m^3 using 15% (w/w) NaOH. They also tested mixtures of aluminium with 5% (w/w) NaOH, obtaining the maximal production of hydrogen (3.22×10^{-3} m^3) with a CaO:Al mass ratio of 0.1; best performance was obtained at 2000 kgf cm^{-2}.

Shkolnikov et al. [67] presented a 2-W cell-phone consisting of a micro fuel cell and a micro generator for hydrogen based on the aluminium-water reaction. Each gramme of aluminium produces 1.2 -1.8 Wh of electrical energy. In their experimental work they examined three ranges of current density: low current density, i.e. <200 mA cm^{-2}; medium current density, 200–500 mA cm^{-2}, and high current density, >500 mA cm^{-2}. The micro fuel cell used was of the air–hydrogen polymer electrolyte membrane type, the air being supplied by a micro fan which was itself energised by the micro fuel cell.

Wanga et al. [68] used a mini-reactor containing an aqueous sodium hydroxide solution and strips of an alloy consisting to 99% (w/w) of aluminium, connected to a fuel cell, to constitute a portable device.   In their work they tried NaOH concentrations of 9%, 17% y 25% (w/w); with the latter concentration they observed the maximum rate of hydrogen production, 247 ml min^{-1}, at an initial temperature of 20°C; once this was coupled to the cell, the latter used hydrogen at a rate of 40 ml min^1, producing power values of up to 0.15 W.

In an attempt to use lower-cost aluminium for hydrogen production, Silva et al. [69] used aluminium from empty soft-drink cans. To speed up the reaction they used 2 M NaOH, removing the paint cover of the cans with sulfuric acid, then cutting them into strips to introduce them into the reactor, which produced experimentally 0.049 moles of hydrogen per gramme of aluminium. This hydrogen was then used in a PEM-type fuel cell. The oxygen for the fuel-cell operation was obtained by water electrolysis energized by

photovoltaic cells. The fuel cell worked with efficiencies of up 10.14%, and achieved a cell voltage of 150 mV.

A portable generator of 2050 mL capacity has been described by Fan et al. [70], charged with Al-Bi-NaCl, in which the aluminium and the bismuth were in powder form (13 microns) mixed with sodium chloride particles. The mixtures originally evaluated were Al with 10 wt% Bi and 1, 3, 5, or 10 wt% NaCl, where the composition Al-10wt.%Bi–5wt.% NaClgave the best hydrogen yield (1063 mL/g Al). Later experiments examined the addition of zinc, when the highest rate of hydrogen production (1026 mL/g Al) was obtained with the mixture Al-10 wt.%Bi-1 wt.%Zn-2 wt.%NaCl. The authors propose this generator as suitable for use with hydrogen fuel cells.

4.3. Power plants

Vlaskin et al. [71] designed a co-generation power plant in which they used aluminium powders with mean particle sizes of up to 70 μm as the main fuel and water as the main oxidizing agent. The plant can function autonomously (i.e. without connection to the electrical net), without ceasing production of hydrogen, electrical energy, and heat. One of the key components of the pilot plant is water-aluminium in a high pressure reactor projected for hydrogen production at a rate of 10 nm^3 h^{-1}. The hydrogen formed flows through a condenser and a dehumidifier with a dew point of -25°C, and enters then a 16-kW hydrogen-air fuel cell. Using 1 kg of aluminium the experimental plant produces 1 kWh of electrical energy and 5 – 7 kWh of heat. Total efficiency of the power plant is 72%, and electrical efficiency is 12%. The electrical efficiency of power plants based on the aluminium-water reaction can be raised by developing devices which use vapour-hydrogen at high temperature to produce electrical energy. They reported that the cost of electrical-energy production in power plants fuelled by aluminium is comparable to the energy costs involved in power generation via the traditional liquid hydrocarbons, while energy generation based on aluminium is a more ecological option.

Rosenband and Gany [72] carried out a parametric study on the aluminium-water method, using a special type of aluminium powder activated by a thermo-chemical process involving a small proportion of a lithium-based activator [73]. The experiments showed a rapid, sustained self-starting reaction between aluminium and water, proceeding even at room temperature, with hydrogen yields of virtually 100% under appropriate conditions. The method demonstrates a safe and compact method of hydrogen storage (11 wt%, based on aluminium). They propose that possible applications would be in fuel cells, as well as in land and sea traffic. The rate of the reaction is independent of the type of water (distilled water, tap water, seawater). The apparent activation energy of the process is about 16.5 kcal/mol.

Silva et al. [74] studied the recycling of aluminium for green energy production, producing high-purity hydrogen gas by the reaction between aluminium and sodium hydroxide at different molar ratios. The results showed acceptable hydrogen yields of sufficient purity for use in PEM fuel cells for electricity generation. A test with 100 aluminium cans reacting

with caustic soda showed that hydrogen production would be possible with a scale-up to 5 kWh in few hours. This work is environmentally friendly and shows that green energy can be produced from aluminium residues at low cost. The hydrogen was easily liberated through a spontaneous chemical reaction, and at relatively low cost, through contact of aluminium from discarded cans with aqueous sodium hydroxide solution. They obtained hydrogen of high purity, which they used in a commercial fuel cell to produce electricity. The hydrogen was produced from a recyclable material, without input of energy and without any additional release of contaminants to the air. They also successfully used the by-product obtained, $NaAl(OH)_4$, to produce an aluminium hydroxide gel to treat water contaminated with arsenic.

Zhuk et al. [75] investigated the generation of electricity using low-cost aluminium, and found that suppressing parasitic corrosion while at the same time maintaining the electrochemical activity of the metal anode is one of the main problems affecting the energy efficiency of aluminium-air batteries. The need to employ aluminium alloys or high-purity aluminium causes a significant increase in the cost of the anode, and therefore in the total cost of the energy produced in the aluminium-air battery; this limits possible applications for this type of power source. They stated that the process of parasitic corrosion is itself a possible method of hydrogen production. Hydrogen produced in this manner in an aluminium-air battery can be used in a fuel cell or burnt to produce heat. Different anode materials would be suitable, such as commercial aluminium, aluminium alloys, or secondary aluminium, which are much cheaper than special alloys for aluminium anodes or high-purity aluminium. Their work consisted mainly in a comparison of the cost of energy production with commercial aluminium alloys, high-purity aluminium, and a special Al-In anode alloy, as anode materials for an aluminium-air battery and for the combined production of electrical energy and hydrogen.

Davoodi et al. [76] tested a microscopic device, based on the principles of scanning electrochemical microscopy (SECM), for collecting electric energy off the surface of an aluminum alloy, AA3003, immersed in 0.01 M aqueous sodium chloride. Using a nanometer-scale atomic-force microscope (AFM), the probe would gather the electrochemical current on the aluminium surface, searching for the regions of highest current density. Their results are interesting from a mechanistic point of view, as they document a large variation in local current densities (from 0.45 pA μm^{-2} for matrix regions to 14.2 pA μm^{-2} for trenches at intermetallic particles); they probably do not hold out realistic prospects for using this method in an economic sense for energy production.

According to Namba et al. [77] the process of remelting of scrap aluminium produces a slag which contains not only metal oxide, but also other by-products. He reported that in Japan 0.35 million tons of this dross are produced yearly. It is remelted to recover aluminium metal with a concentration of between 10 and several dozen percent by weight. Hiraki and Akiyama [78] proposed a novel system to treat aluminium residues, such as this slag. They evaluated from the point of view of the life cycle the total exergy loss (EXL) in comparison to the EXLs attendant on the co-production of 1 kg of hydrogen at 30 MPa and 26 kg of

aluminium hydroxide. The exergy flow diagram shows that the exergy of aluminium residues containing only 15% of the metal by weight is still large, while the exergy of pure aluminium hydroxide is relatively small. The exergy of the proposed system (150.9 MJ) is inferior by 55% compared to the conventional system (337.7 MJ), in which the gas compressor and the production of aluminium hydroxide consume significantly more exergy. The results also show that the exergy analysis should be applied to the life-cycle assessment (LCA) as a critical consideration for practical use, additional to the conventional LCA on the emission of carbon dioxide. When this concentration becomes smaller than 20% by weight due to the remelting, the slag is chemically treated as an inocuous substance by methods such as high-temperature fusion in the electric arc, at a cost of US$200-300 per tonne.

5. Patents on reactors for the aluminum-water reaction

Houser [79] developed an invention on heating systems, and more specifically a device in which the chemical oxidation-reduction reactions would proceed producing heat, but without flame formation, in contrast to most heating systems. The system has a housing whose lower part holds the liquid reagent, e.g. NaOH solution. The solid reactant, e.g. aluminium metal, is immersed in the solution to produce heat and gaseous product, e.g. hydrogen. The position of the container within the deposit is regulated to control the extent of immersion, and the solid reagent inside the container can react with the liquid, producing heat. The hydrogen gas produced rises to the top of the conical cover and exits via a topside conduit to be washed with water and then transferred to storage or used directly via combustion. The water bath insulates the interior of the system, thus precluding combustion of the hydrogen in the system. The sodium aluminate produced in the reaction forms a mud, which is diverted to the drain by an inclined conical wall in the lower part of the housing. To start the system functioning, the lower part of the housing is filled with the solution and the container is raised above the level of the solution. To activate the heating system, the solution is first ohmically heated by an electrical resistance to about 140°C for total efficiency.

Houser [80] describes another gas generator which utilizes spherical pieces of a solid reactive material in contact with a second, liquid reagent. The spheres are moved through the reaction chamber via inclined channels with holes, which could be made e.g. from screen mesh tubing. The liquid reagent is sprayed from dispersion nozzles onto the spheres which move upward via the channels. The solid residues are removed from the spheres through the rolling action of the spheres against the channel walls and washed away by gravity. The liquid reagent is again conducted to a sump, whence it is pumped through a filter to remove the waste product of the reaction; it then is returned to the nozzles in the reaction chamber. The concentration of the liquid reagent is regulated through a sensor in the sump, which controls the addition of concentrated make-up solution. The temperature of the liquid reagent is also controlled by a sensor in the sump or a thermostatic valve in the sediments filter, allowing the liquid to flow through an indirect heat exchanger. The gas generated is delivered from the reaction chamber by its own pressure. Not surprisingly, the preferred

embodiment of the invention is the production of hydrogen from aluminium spheres and sodium hydroxide solution.

Andersen and Andersen [81] built a prototype device to produce hydrogen by making aluminium react with water in the presence of sodium hydroxide at between 0.26 M and 19 M. The reaction takes place with effervescence at the metal surface; at the same time, a precipitate collects at the bottom of the container. The zone of effervescence is kept separate from the zone where the precipitate collects. This reduces the possible hindrance of the hydrogen-generating reaction by the precipitate. Satisfactory results are obtained with sodium hydroxide concentrations between 1.2 and 19 M and at temperatures from 4°C to 170°C, with best performance seen at NaOH values between 5 and 10 M and solution temperatures around 75°C.

Andersen and Andersen [82] also constructed another prototype which produces heat and hydrogen gas, all at ambient temperature. Here, aqueous NaOH (18 wt%) half-fills an expandable container which adjusts to the momentary pressure and temperature of the reaction by expanding and contracting, thus controlling the level of immersion of a fuel cartridge containing aluminium filings or shavings or aluminium foil, to manage the intensity and duration of the reaction. The upper part of the container is built from flexible material and joined to the support of the fuel cartridge, so that, as the hydrogen is produced, the internal pressure in the container increases, moving the upper lid and thus lifting the aluminum out of the aqueous sodium hydroxide, thereby stopping the chemical reaction. As the hydrogen is consumed, e.g. by combustion, the internal pressure in the container drops, and the aluminum again gets in contact with the lye, and hydrogen production restarts. This cycle repeats itself until the aluminium is used up.

Troczynski [83] described a hydrogen-generating system based on hydrolysis of a composite aluminium material, at a pH close to neutral, to supply hydrogen to fuel cells or other devices. The process of use involves: (a) Supply of water to the composite material in the reactor vessel to produce the hydrogen (b) Passage of the hydrogen formed from the reactor to a buffer vessel, and (c) liberation of the hydrogen from the buffer vessel to the fuel cell, at a second, lower, pressure which is compatible with the fuel cell. Several reactor vessels and several buffer vessels are monitored by pressure sensors and connected by processor-controlled valves to assure a continuous supply of hydrogen to the fuel cell.

Fullerton [84] developed a recyclable hydrogen generator which uses aluminium, an alkali hydroxide, and water, connected to a user, which could be an internal-combustion engine, a turbine, or a fuel cell. The hydrogen generator safely supplies the hydrogen demand at atmospheric pressure, and it can be stored anywhere at low cost, as it is safe and inert.

6. Conclusions

Interest in hydrogen as an energy carrier is based on considerations of the finite nature of our hydrocarbon resources and of the worldwide deleterious effects of the carbon dioxide emitted during hydrocarbon-based energy production. In this context, the aluminium-water

reaction shows interesting possibilities as an energy-providing small or mid-scale reaction. In contrast to gasoline-air based systems, which benefit from the ubiquitous presence of air, the aluminium-water reaction requires that the latter be specifically supplied or brought along; however, the ready availability of water at most places minimizes the importance of this consideration.

An attractive feature of the aluminium-water reaction as a way to produce hydrogen gas on demand is its essential simplicity. Obviously, in its most basic form, the reaction is fundamentally hampered by passivation of the metal, but this can be overcome by the use of strongly alkaline conditions. However, the corrosiveness of such conditions is a distinct drawback; for this reason, extensive research has centred in recent years on means of maintaining an active metal surface in aqueous conditions at neutral or near-neutral pH, e.g. by the use of aluminium alloys. Research in these aspects is likely to remain important in the immediate future.

Large-scale application of the aluminium-water reaction appears less promising and is unlikely to replace to any significant extent the more established modalities, e.g. energy storage in battery banks.

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