Article

Analysis of Valorization Process of Aluminum Breakage Scraps to Obtain Green Hydrogen

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Abstract: In this article, it is proposed to use aluminum breakage scraps to obtain Green Hydrogen through the aluminum-water reaction with caustic soda as a catalyst with experimental research. From this exothermic reaction, both hydrogen and the heat generated can be used. Due to the low price of aluminum chips, this allows us to produce Green hydrogen below the current price that is obtained using renewable energy sources and electrolyzers. On the other hand, we have developed a process that is sustainable since it is obtained as alumina and caustic soda waste that can be reused. This alumina obtained, once filtered, has high purity which allows us to produce high-quality primary aluminum without the need to use bauxite and reducing the production of red sludge. A comparative study-analysis has been carried out of two of the types of forms in which the most common aluminum is presented in the industry to analyze which one performs better by studying key factors such as the hydrogen produced, and the waste generated during the process. Finally, the mathematical model has been defined to be able to control the flow based on different key parameters such as temperature, molarity, and geometry. Undoubtedly, the study that we present represents a milestone for the recovery of metallic aluminum waste and may be of great interest to industries that use aluminum in their processes, such as recuperators, but also the vehicle or aerospace industry.

Keywords: Metal waste valorization; aluminum breakage scrap; green hydrogen; hydrogen-controlled generation

1. Introduction

Different industries use hydrogen in their industrial processes, such as heat treatments, synthesis of ammonia and hydrochloric acid, water treatments, or generators of electric energy using fuel cells, that could eventually be interested in not depending on distributors of industrial gases.

Furthermore, there is currently a lot of interest in producing green hydrogen, that is, without emitting CO_2 [1]. The most widely used systems are those that use the electrolysis of water using renewable energies and electrolyzers [2]. The problem with these systems is that it depends on the price of electricity, the amount of hydrogen required and the effectiveness of the electrolyzer, so the cost of hydrogen generated in a medium-size demand and for an efficiency greater than 60% is of the order 2.5-7 \$ / kg H_2 [3].

At present, various systems are being studied for obtaining hydrogen from the aluminum-water reaction [4]. The advantage of this method is the possibility of obtaining high purity hydrogen from aluminum waste [5], in a reactor located in the customer's own company, with no need of using high-pressure hydrogen storage tanks.

When studying whether this system is profitable, it is usually done from an energy point of view, assuming that aluminum is manufactured only to generate hydrogen. But, when it is obtained from the aluminum wastes that hydrogen is be obtained. In this study, the economic aspect is more valued and it is interesting to note that the price of the aluminum machining chips [~ 0,6 \$/kg (LME 2020)] is lower, compared not only to the first and second melt, but also to other types of aluminum scrap, so it could be used for green hydrogen production.

This system is also completely sustainable since Al_2O_3 can be converted into top-quality aluminum with the contribution of renewable energy, avoiding its extraction, transport, and treatment of bauxite ore, which represents 5.6 kWh / kg Al, and the management of waste. treatment alkalis (red sludge).

One of the current methods experimented to obtain hydrogen from metallic liquid aluminum using gallium or activated Ga-In-Sn-Bi alloys with water, but the system requires preparation, is expensive and the waste must be processed [6].

Another of the methods used to facilitate the aluminum-water reaction is to introduce aluminum into an alkaline solution to remove the surface oxide layer and subsequently the different layers of aluminum hydroxide created [7]. There are several cases of industrial prototypes where this technology is applied [8], although it is usually based on high purity aluminum powder, a size in the micron range, o and very high price [9], compared to machining chips. In such prototypes, the aluminum, which enters the reactor, is usually dosed to control the flow rate of hydrogen generated [10]. Generally, in industrial processes or fuel cells, the flow rate is to be constant over time, to stop the flow in case of a shutdown, or to increase it in case of increased production [11].

From a technological point of view to dose a solid, especially in the form of a chip, is more difficult than to dose a liquid [12]. That's why a system that doses liquid is preferred. On the other hand, when the aluminum chip is contacted with water in an alkaline medium, a constant flow of hydrogen is not produced. Initially, a very high flow rate is obtained, and it decreases as time passes [13]. In case that a certain flow is needed, then a reservoir is required to store part of the initial hydrogen or the remainder in the event of a shutdown when operating this way. This reservoir could be avoided or reduced with a system that exactly generates the required flow and that could react almost immediately in case of a stop, as the one proposed in this study. Another drawback of the aluminum-water reaction in the alkaline medium is that, although the hydrogen obtained is of high purity, it usually sweeps along some particles of sodium hydroxide (NaOH) and water vapor [14], which often makes filtering difficult.

The aluminum is to be introduced into a reactor and the sodium hydroxide solution will be dosed to achieve the required hydrogen flow rate. A very common way of proceeding with this type of process is to flood part of the reactor with the NaOH solution [15]. In this type of systems, the hydrogen flow rate is hardly constant [16], with the risk that in case of a shutdown, when the liquid is removed from the reactor, aluminum hydroxide plates may appear on the wetted surface of aluminum, which slows down the restart of a new reaction and makes

it more difficult [17]. Besides, a blockage in the liquid outlet from the reactor, due for example to aluminum chips, other metals, or crystallized aluminum hydroxide, could force the reaction to occur, the production of hydrogen would excess and therefore the reactor could be damaged due to overpressure [18].

This research proposes a method for obtaining hydrogen from aluminum chips in a controlled manner in an alcoholic medium [19] with isopropyl alcohol, by dosing sodium hydroxide solution 7.5M [20]. A theoretical-experimental model will be proposed to define the hydrogen flow rate as a function of the size of the chip, the active surface, the molarity, and the temperature of the solution. The way the alcohol affects the reaction will also be described. A comparative study of the hydrogen flow rates obtained with different types of machining chips, as well as the performance of the reaction, will also be carried out. Finally, the purity of the hydrogen and the derived by-product, alumina (Al_2O_3), will be analyzed.

2. Materials and Methods

2.1. Aluminum

2.1.1. Aluminum plate(A1)

To get the theoretical-experimental model, a 0.5mm thick aluminum plate was used, according to ISO 209: 2007 Al 99.5 and whose characteristics are shown in *Table 1*.

Table 1. Designation and composition of aluminum ISO 209 Al 99.5 of the plate.

Aluminum	Si(%)	Cu(%)	Zn(%)	Fe(%)	Mn(%)	Others (%)	Al(%)
A1	0,25	0,05	0,1	0,4	0,05	<0,05	99,5

2.1.2. Aluminum chips(A2&A3)

To carry out the comparative study of the aluminum chips from the industry, turning chips of approximately $20 \times 5 \times 0.5$ mm^3 were selected, being A2: aluminum chips from the automotive industry and A3: aluminum chips from the aeronautical industry, whose characteristics are shown in *Table 2*.

Table 2. Designation and composition of aluminum chips from the automotive industry (A2) and the aeronautical industry (A3).

Aluminum	Si(%)	Cu(%)	Zn(%)	Fe(%)	Mn(%)	Others (%)	Al(%)
A2	5	1,5	0,7	0,5	0,15	<0,05	92
A3	0,5	1	5	0,2	0,1	<0,05	94

2.1.3. Pure grainy Aluminum (A4)

It is necessary to use pure grainy Aluminum with a diameter less than 1 mm as a reference in the results since it will not be affected by passivation due to its size, purity, and shape. Also, this will be used as a reference to evaluate the results of the purity of the waste, aluminum hydroxide (PANREAC 141098.1611), the characteristics are shown in *Table 3*.

Table 3. Designation and composition of pure grainy aluminum taken as reference(A4).

Aluminum	Si(%)	Cu(%)	Zn(%)	Fe(%)	Mn(%)	Others (%)	Al(%)
A4	-	-	-	-	-	<0,05	99,7

2.2. Sodium hydroxide

The study was carried out with solutions of sodium hydroxide 7.5 M [20], from 50% solutions (PANREAC 142404.0716) and distilled water.

2.3. Alcohol

The alcohol used is 99% isopropyl alcohol [16] and whose characteristics are shown in *Table 4*.

Table 4. Designation and composition of alcohol used in the tests.

Alcohol (99%)	Formula	$T_{boiling}$(ºC)	Density (g/cm³) at 20ºC	Solubility in H_2O
Isopropyl alcohol	C_3H_8O	83	0,79	miscible

It is important to highlight that the boiling temperature of the alcohol has to be higher than 60°C since the optimum aluminum-water reaction temperature is 60°C [21] and therefore the control of these vapors in the condenser becomes easier.

3. COMPONENTS AND METHODOLOGY USED IN TESTS

3.1. Determining the theoretical model

A test has been carried out to find the theoretical model, to know how aluminum chips react in a 7.5 M caustic soda solution, with and without isopropyl alcohol. As shown in *Figure 1*, the test was carried out with the following components: a 500 ml flask with one outlet, hermetically sealed, and with the outlet connected to a calibrated test tube, filled with water, by a silicone tube; a heater to maintain the double boiler temperature at 25°C in one of the tests and 60°C in the other one; a calibrated test tube to evaluate the volume of hydrogen produced, and a chronometer to calculate the flow rate.

The selected aluminum has always been of type A1 (according to *Table I*), all tests being carried out in the same way. The water was first heated to a test temperature of 25°C or 60°C in a 200 ml 7.5 M NaOH solution (with or without 100 ml of isopropyl alcohol, according to the test) in a double boiler or water bath heater. Then, the aluminum samples were introduced into the flask while keeping the temperature constant, and the flask was capped to make it airtight. The aluminum reacted with the solution and some hydrogen was generated. The hydrogen was led to a calibrated test tube by a silicone tube. The measure of the volume of generated hydrogen was taken every minute at a temperature of 15°C. The test ended when all the aluminum was consumed. Two tests were performed with each sample, getting the mean values, and repeating the measurement if the variation exceeded 10%. In some tests, the dimensions the thickness of the chips were measured every minute with a centesimal micrometer (expanded uncertainty U=0.005 mm).
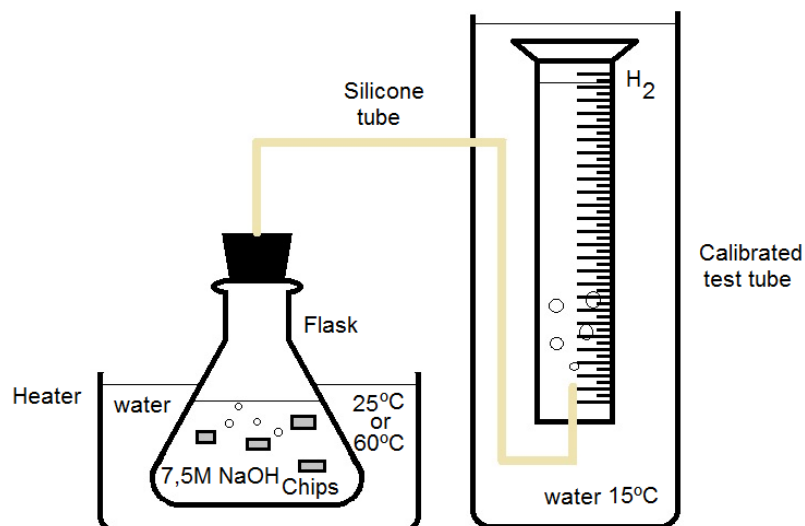
Figure 1. - Draft of the experimental equipment used for theoretical model determination test.

4. Tests

4.1. Test 1: Effect of chips size

In test 1 two experiments were carried out to compare the generation of hydrogen by a reaction of water-aluminumA1 in a 7.5M NaOH solution, at 25°C in plate [sheet] or chip [bit]format. A 20x30x0.5 mm³plate was first tested and then a set of 104 chips of 2x2x0.5 mm³ were tested too so that in both tests both samples had the same initial contact surface (1240 mm²), see in table 5.

Table 5. A1 plates and chips features.

Typology	Quantity	Dimensions (mm³)	Weight (g)	Initial contact surface (mm²)
Plates [sheets]	1	20x30x0,5	0,788	1240
Chips[bits]	104	2x2x0,5	0,534	1240

A chip thickness of 0.5 mm has been chosen since it is usually the one chosen in finishing machining and as it will be seen later, it does not influence the active surface. An increase in this value would increase the reaction time but would not vary the flow achieved significantly.

4.2. Test 2: Temperature effect

In test 2 the effect of temperature on hydrogen flow generation was compared. As verified in the previous test, the reaction time depends on the plate thickness regardless of the shape of the plates or chips. Therefore, a 20x30x0.5 mm³ plate was used for the test, and the temperature effects were experienced at 25°C and 60°C.

4.3. Test 3: Effect of adding alcohol

In test 3 the effect of adding isopropyl alcohol in the NaOH solution was compared. A 20x30x0.5 mm³ aluminum plate was used at 60 ° C with and without propyl alcohol. This allowed us to see the effects of the addition of alcohol.

5. Hydrogen Generation Reactor from Chips

5.1. Hydrogen Generation Procedure

Hydrogen generation was carried out by using a covered 20-liter reactor in glass, by using water at 60°C as a heating fluid throughout the experiment to maintain the inside temperature between 60°C and 65°C. As shown in *Figure 2*, the A2 and A3 aluminum chips were introduced together with enough alcohol to cover them, namely 100 ml. The reactor was fed with a 7.5 M sodium hydroxide solution at a constant flow rate of 10 ml/min through a Heidolph PD-5001 one head peristaltic pump with a silicone tube of 6.3/9.5 mm diameter. The hydrogen generated in the aluminum-water reaction was circulated by a water-cooled condenser to remove any alcohol vapors. To ensure that hydrogen did not carry alcohol, it was passed through a water filter. The hydrogen was filtered with a silica gel trap to remove any remaining moisture and the flow rate was subsequently measured with a volumetric gas meter. Both the sodium hydroxide solution flow rate and the weight of the aluminum chips as well as the amount of alcohol were specified in each of the tests performed.

The hydrogen flow rate was measured using a RITTER TG20/6 volumetric gas meter, and time readings were also carried out for every liter, and the total volume of hydrogen generated was set. The objective of the experiment is to compare the results obtained with each one of these two types of chips to choose the most suitable one for hydrogen generation.
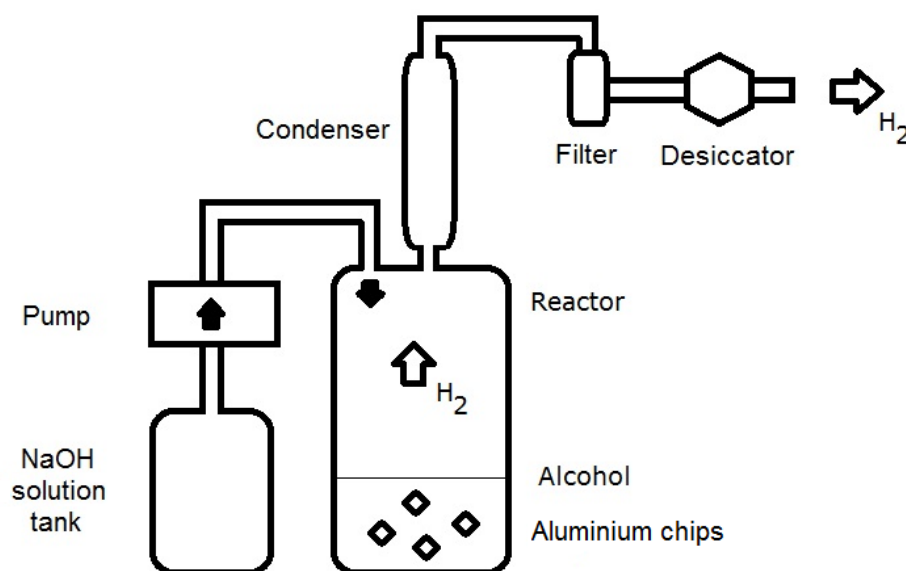

Figure 2. - Draft of the experimental equipment used for the production of hydrogen.

5.2. Analysis of hydrogen purity

To determine the hydrogen purity, several samples of one liter of hydrogen generated from aluminum A2 were collected in a Tedlar bag after purging the gas. The hydrogen obtained was then analyzed by an "Agilent 3000ª" gas microchromatograph with 3 independent modules with a thermal conductivity detector (TCD) and columns for measuring light gases (molecular sieve), light hydrocarbons (plot U), and oxygen compounds (Stabilwax). The analysis was carried out by directly injecting the sample into the equipment and obtaining the results from a calibration of the equipment from 99.999% pure hydrogen. Three tests were performed for each one of the samples collected.

5.3. Analysis of aluminum hydroxide purity

To find the aluminum hydroxide purity, several samples of sodium tetrahydroxyaluminate were collected and precipitated as $Al(OH)_3$ with hydrochloric acid. Subsequently, it was cleaned to eliminate any trace of soluble salts that might have formed during the reaction with the acid. The samples were then dried in an oven at 1000°C, for 30 minutes,

to obtain Al_2O_3, and finally, the purity of the aluminum oxide obtained by a mass spectrometer was analyzed in an external laboratory.

6. Theoretical Kinetic Model

6.1. Chemical reactions

A diffusion phenomenon occurs on the aluminum-NaOH surface. We will address this phenomenon from a chemical point of view. The reaction to obtain hydrogen from aluminum and water [21] is given by *equation1*.

$$Al\ (s) + 3\ H_2O\ (l) \rightarrow\ \ Al(OH)_3\ (s) + 3/2\ H_2\ \ (g)$$

$$\Delta H = -278\ kJ/mol\ H_2 \tag{1}$$
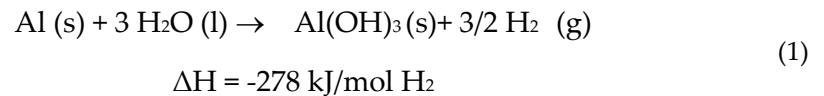
Since the aluminum hydroxide is solid, it creates a surface layer that prevents water from reacting with aluminum, so it makes it inactive. To prevent inactivity, the reaction must be carried out with an alkaline solution (NaOH) so that the aluminum hydroxide is converted into aqueous sodium tetrahydroxyaluminate according to *equation 2*.

$$Al(OH)_3\ (s) + NaOH\ (aq) \rightarrow Na\ Al\ (OH)_4\ (aq) \tag{2}$$

To formulate the kinetic model, it is assumed initially, as a hypothesis, that there will be enough aluminum active surface area, which reacts with water so that the hydrogen flow rate depends exclusively on the added water flow rate [19]. This hypothesis will be used only as a starting point for the study since this area might be reduced by the partial inactivity of the area due to the appearance of aluminum hydroxide in the form of bayerite [18]. Furthermore, in our case, this is more noticeable in the case of chips than in the case of grains, since the contact with the sodium hydroxide is lower because of the shape, and therefore also the reaction to get sodium tetrahydroxyaluminate according to the *equation2* is lower. This active surface decreases as time passes since the aluminum is transformed into aluminum hydroxide, depending also on the geometric shape of the original product. The originality of this study is that this surface has been modeled, for the simple prismatic chip shape. Finally, based on the experimental data, it has been calculated what the active surface should be so that the limiting reactant is water, or aluminum, in the hydrogen output.

6.2. Theoretical Hydrogen Flow

The hypothesis of enough active aluminum surface

The theoretical hydrogen flow rate $Q_{H2,t}$ obtained according to *equation 1*, for any aluminum shape, as a function of the water flow rate Q_{H2O}, with a density of ρ_{H2O} and an atomic weight of water of M_{H2O}, can be written according to equation (3), assuming an ideal gas performance [20]. The fundamental hypothesis is based on the fact that there is enough active aluminum surface.

$$Al(OH)_3\ (s) + NaOH\ (aq) \rightarrow Na\ Al\ (OH)_4\ (aq) \tag{3}$$

The hypothesis of not enough active aluminum surface

The theoretical hydrogen flow rate $Q_{H2,t}$ obtained according to *equation 1*, for a sufficient water flow rate, as a function of the aluminum active surface $S_{Al,t}$, the reduction of thickness as a function of time e, the density ρ_{Al}, and the atomic weight M_{Al}, can be written approximately according to equation (4), assuming an ideal gas performance [20]. The fundamental hypothesis is since there is not enough active aluminum surface to react with the supplied water flow.

$$Q_{H2,t} \approx \frac{3}{2} \frac{\rho_{Al}}{M_{Al}} \left(\frac{RT}{P}\right) (S_{Al,t} \cdot e) \tag{4}$$

6.3. Active aluminum surface

Aluminum waste in the grainy form

When the waste is grain-shaped, the particles are considered to be spheres of radius R, same size, and it is assumed that the aluminum alloy is homogeneous with purity η and density ρ_{Al}. The depletion of the radius is assumed to be constant as a function of time, its active surface being a function of the initial aluminum mass $W_{Al,0}$, and time, according to *equation 5* described and developed in the bibliography [23].

$$S_{Al,t} = \left(\frac{3W_{Al,0}\,\eta}{\rho_{Al}}\right)\frac{R_t^2}{R_0^3} \tag{5}$$

Aluminum waste in chip shape

Assuming that the chip is an ideally prismatic shape, a model that describes the active aluminum chip surface as a function of time has been developed.

If we consider an aluminum machining chip with dimensions $L·a·p$, where p is the cutting depth, a is the feed and L is the length (*figure 3*), and assuming, as assumed in the previous section, that there is a constant reduction of the surface thickness e as a function of time (in minutes), the depletion of the chip will be a function of time t (in minutes) and will be applied on all surfaces of the chip until the thickness p is consumed, which will always be the smaller dimension.
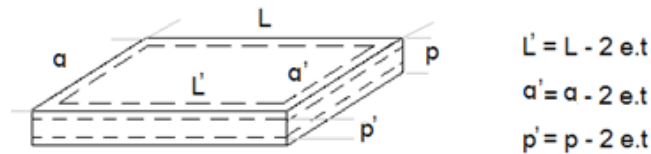

Figure 3. - Theoretical representation of the thickness depletion "e" as a function of time "t" of a machining chip due to the aluminum-water reaction.

The active surface as a function of the initial aluminum mass, purity, and density are described according to *equation 6*.

$$S_{Al,t} = \frac{2W_{Al,0}\eta}{\rho_{Al}\,L\,a\,p}[4et(3et-(L+a+p))+L\,p+L\,a+pa] \tag{6}$$

Experimental confirmation of this formula was carried out, by introducing prismatic aluminum *A1* chips (see *Table I*), with dimensions 20x30x0.5 mm^3 in a 7.5M NaOH solution, keeping a constant temperature at the water bath. As the reduction of the thickness depends on the temperature, this has been analyzed at 25°C and 60°C, and it has been concluded that the calculated active surface exactly matches the experimental active surface, and it is linearly reduced [19]. The experimental average reduction or depletion is shown in *Table 6*.

Table 6. Reduction of aluminum A1 thickness as a function of temperature in 7.5M NaOH.

Temperature (°C)	Thickness reduction (mm/min)
25	0,00117 ± 0,00003
60	0,01473 ± 0,00003

Of course, the lifetime of the chip, from the time it begins to react until it is completely consumed, depends on its smaller dimension, ie its thickness p. Since the thickness of the chip is very small, the reduction of the upper and lower faces, L·a, is minor, so that the active surface would go from a noteworthy value to zero abruptly, when the thickness $p'=p-2et$ equals zero. This happens gradually since in the last phase the chip floats and

disappears from the ends towards the center. The exact flow rate obtained as a function of time $Q_{H2,t}$, improving *equation 4*, is determined by *equation 7*.

$$Q_{H2,t} = \frac{3}{2}\frac{\rho_{Al}}{M_{Al,t}}\left(\frac{RT}{P}\right)(S_{Al,t}.e - 4\,e^2\,((p - 2et) + (a - 2et) + (L - 2et) - 2e)) \quad (7)$$

where the total theoretical volume of hydrogen V_{H2} obtained at a time t = n [minutes] is given by *equation 8*:

$$V_{H2} = \frac{3}{2}\frac{\rho_{Al}}{M_{Al}}\left(\frac{RT}{P}\right)\sum_{t=0}^{n}(S_{Al,t}.e - 4\,e^2\,((p - 2et) + (a - 2et) + (L - 2et)) \quad (8)$$

7. Results and Discussion

7.1. Result of test 1: Effect of chips size

The generation of hydrogen from one single sheet was studied in the first test, and 104 A1 aluminum chips with the same initial active surface area were studied in the second test. In both cases, the surface was 1240 mm², in a 7.5M NaOH solution (without Alcohol) at a water bath temperature of 25°C. The result of the tests are shown in *figure 4*, as well as the theoretical values according to *equation 8*.
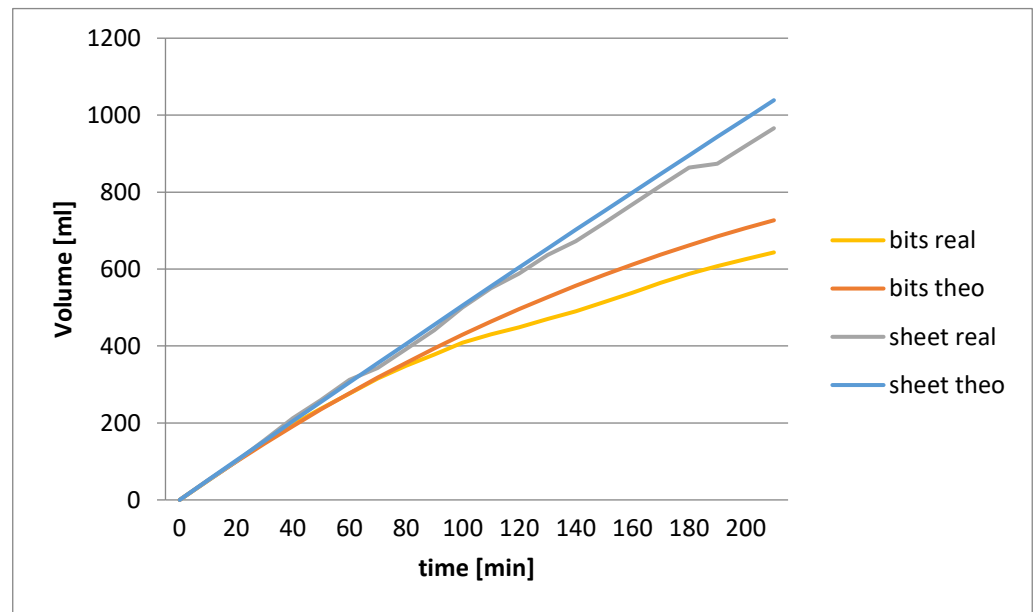

Figure 4. - Comparison of the hydrogen volume generated from 104 sheet metal chips of 2x2x0,5mm³ (bits) and a plate of 20x30x0,5 mm³ (sheet) of aluminum A1, of the same initial active surface 1240 mm² in a 7.5M NaOH (non-alcohol) solution at a bath temperature of 25°C.

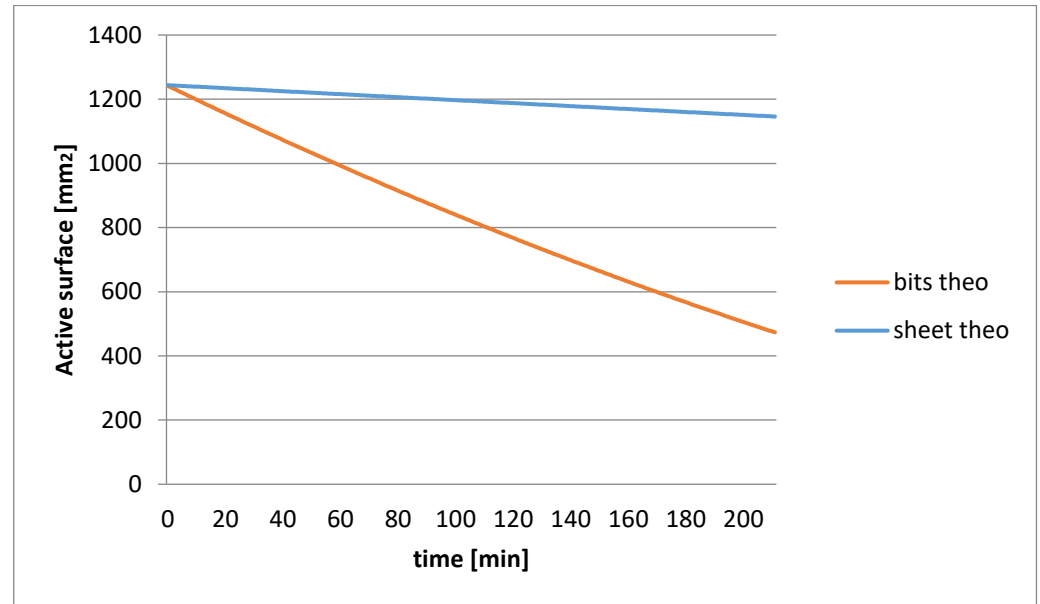The active aluminum surface, given in *equation 6*, is shown in *figure 5*.

Figure 5. - Comparison of the theoretical active aluminum surface for 104 sheet metal chips of 2x2x 0,5mm^3 (bits) and a plate (sheet) of aluminum A1 of 20x30x0,5 mm^3.

Figure 4. shows how the hydrogen flow is fairly constantly, approximately 5 to 4 ml/min, generated in the plate, while it decreases in the chips. This fact, as seen in *Figure 5*, is because the active surface is reduced faster in the chips than in the sheet. Initially, for both types, there is enough active aluminum surface so that the restricting element is the flow rate of water in contact and the generated hydrogen flow follows *equation 3*. In the case of using chips, after about 30 minutes, the active surface is lower than the critical surface and the hydrogen flow then follows *equation 7*, where the restricting element is aluminum. It is also observed that the reaction time depends on the thickness p, either in the sheet or in the chip format. Therefore, it is important to know the instantaneous active surface to calculate the hydrogen flow rate that can be generated.

7.2. Result of test 2: Temperature effect

Figure 6 shows how temperature affects the hydrogen generation reaction tested on a sheet of Al in a water bath at 25°C and 60°C, compared to those theoretically obtained in *equation 8*. It should be noted that the temperature of measurement of the hydrogen flow rate was 15°C, and therefore, this is the temperature to be entered in that equation.
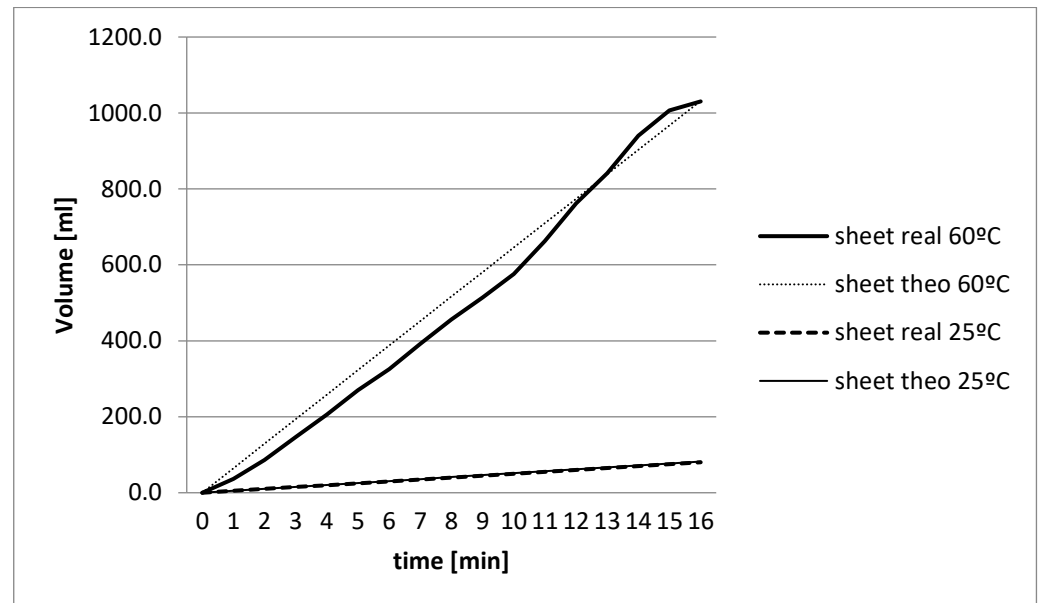
Figure 6. - Comparison of the hydrogen volume generated from an aluminum sheet of 20x30x0.5 mm³ (sheet) in a 7.5M NaOH solution (without alcohol), at a bath temperature of 60ºC and 25ºC.

The temperature directly affects the thickness e depletion as shown in *Table 7*, so the flow rate will be much higher at 60°C.

Table 7. Comparison of the effect of temperature on hydrogen generation.

Aluminum A1 sheet (mm3)	Temperature (ºC)	Thickness depletion e (mm/min)	Time (min)	Average flow rate (ml/min)
20x30x0,5	25	0,00117 ± 0,00003	208	4,7
20x30x0,5	60	0,01473 ± 0,00003	16	64,3

7.3. Result of test 3: Effect of adding alcohol

Figure 7 shows the comparison of the flow experimentally obtained by the addition of isopropyl alcohol in the NaOH solution with that obtained without alcohol. An aluminum sheet of 20x30x0.5 mm³ was used, at 60ºC with and without isopropyl alcohol

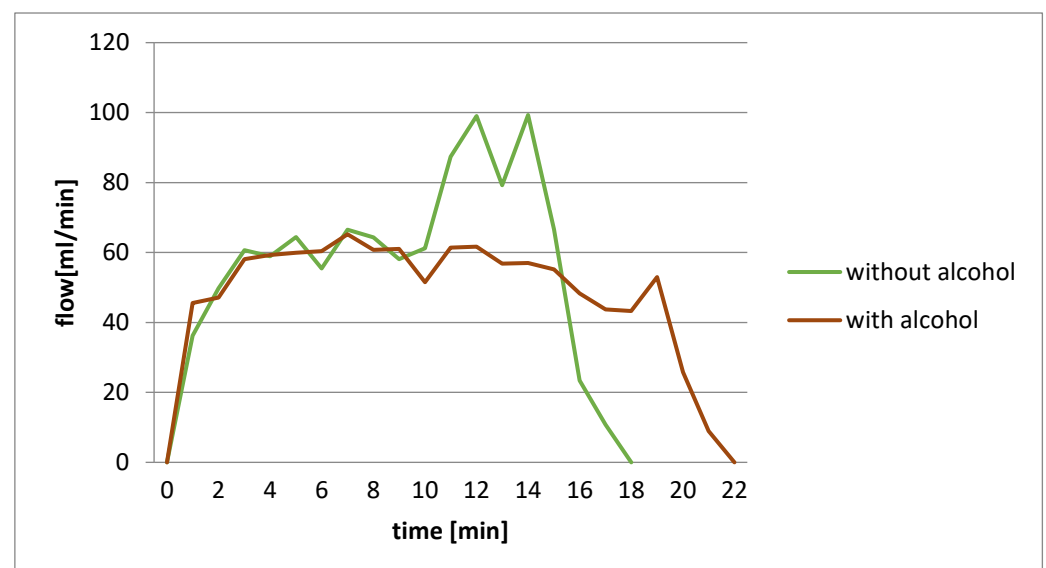**Figure 7. -** Comparison of the hydrogen flow rate generated from an aluminum A1 sheet of 20x30x0.5 mm³ in a 7.5M NaOH solution, with and without isopropyl alcohol in a water bath at 60 ° C.

As the alcohol has a lower density [24] than the NaOH 7.5M solution, two layers or phases are formed initially, and the sheet stays submerged in the NaOH solution at 60ºC. As the temperature increases, the flow rate increases too, and the aluminum-water reaction is exothermic, but since there are two phases, the temperature keeps constant. So, when the sheet floats to the interface due to the loss of thickness, the flow rate does not increase, but it remains constant. In the absence of alcohol in the upper zone of the solution, the temperature increases to 65 ° C due to the reaction (although the bath remains at 60°C), and then the flow rate also increases. In industrial processes, the flow rate should always be as constant as possible, and the alcohol helps to achieve it. When the sheet is so thin as to float in the alcohol, the reaction slows down and the sheet is not consumed until 16 minutes later, generating an insignificant flow. Another advantage of using the alcohol is that the reaction is less active, as the sheet floats away from the interface, between the NaOH solution and the alcohol phase. So the reaction can be stopped by controlling the level of alcohol so that the Aluminum is immersed in it. Finally, the alcohol acts as a filter by not allowing the hydrogen to seep along any NaOH particle.

7.4. Results in the hydrogen generation reactor from different types of industrial aluminum chips

Figure 8 shows the results obtained by reacting different types of chips obtained by machining different aluminum used in the industry, with the 7.5M solution and isopropyl alcohol in the reactor. Those chips are those of automotive aluminum A1 and aeronautical aluminum A2. The same mass of pure granule aluminum A3, with a large active surface, is also reacted, and it is taken as a reference.

It was seen that in the case of chips, the results obtained for pure aluminum with a large surface area, were initially exceeded. This fact is caused by the appearance of impurities in the chips due to the oxides of the components of their alloys [25], which makes the reaction between aluminum and water easier as they cause "paths" in the oxide or Aluminum hydroxide layers formed on the aluminum surface. These paths facilitate the introduction of water through the inactive surface layers, and therefore its contact with aluminum.

After the initial phase, hydrogen flow rates of about 3 l/min were reached, both by using chips and granulate aluminum. This flow corresponds approximately to the one generated from 5.4 ml/min of water (10 ml/min of 7.5 M NaOH) assuming enough aluminum active surface, ie according to equation 3, of 3.5 l/min. This difference in flow is due to the decrease of the contact surface between the NaOH solution and the aluminum surface because of the interaction of isopropyl alcohol.

250 seconds after the reaction has started, the generated hydrogen flow decreases when using chips, due to the decrease of the active surface. This fact does not occur when using granules, with a larger active surface. When using granules, the flow rate remains constant.

550 seconds after the reaction had started, the feed of NaOH solution was stopped by stopping the pump, to check if it was possible to quickly stop the generation of hydrogen by stopping the feed, and the result was affirmative.
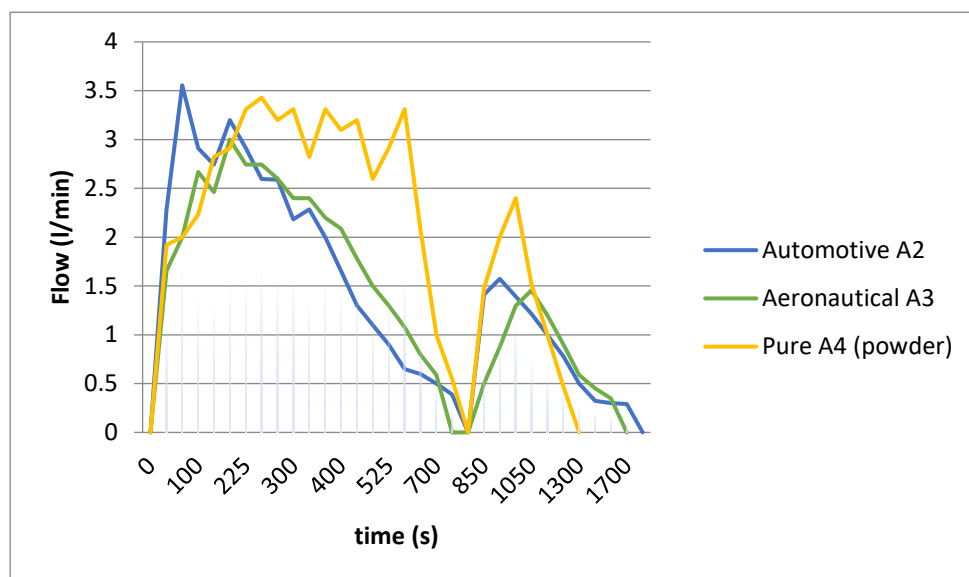
Figure 8. - Comparison of the hydrogen flow generated by automotive aluminum chips A2, aero-nautical aluminum chips A3 in alcoholic medium, and isopropyl alcohol, starting from 30 grams of aluminum and dosing 10 ml/min of 7.5M sodium hydroxide solution, at a bath temperature of 60°C in the reactor. These are compared to the pure granulated aluminum A4 (powder), used as a reference, under the same conditions.

When the reaction restarted, the same flow rate corresponding to the active surface before the interruption was obtained, and only 1.5 liters/min were reached, and it progressively decreased until the aluminum was completely consumed. Since the chips had a larger thickness than the granulate one, the reaction lasted a few seconds longer than the one with the pure aluminum taken as a reference, ending after about 1700 seconds. Afterward, a solution of sodium hydroxide, without alcohol, was added to the remaining aluminum wastes that floated on the alcohol, and it was left there for several hours to quantify all the hydrogen that can be extracted from each type of aluminum.

Table 8 shows the hydrogen obtained in the different cases. In the first column, the resulting hydrogen volume is shown after adding 100 ml of 7.5M sodium hydroxide solution in an alcoholic medium and waiting for the reaction to stop. In the second column, the volume of hydrogen obtained is shown after adding another 100 ml of 7.5M sodium hydroxide solution in an alcoholic medium, ie too much solution, and waiting for the reaction to stop (that is to say, waiting until the process ends). In the third column, the total volume of hydrogen obtained is shown, emptying the reactor but leaving the unreacted aluminum wastes, adding then another 100 ml of solution, but in a non-alcoholic medium, and waiting also for the reaction to stop. Both the process yields and the total yield are related to the hydrogen that could be obtained by stoichiometry with 100% pure aluminum. As proved, the purity of the aluminum and its shape is fundamental for a properly functioning system.

Table 8. Hydrogen flow rate generated for 100 ml of 7.5 M NaOH solution in an alcoholic medium. Hydrogen flow is generated at the end of the process or reaction in an alcoholic medium, isopropyl alcohol. Total flow rate by adding 7.5M NaOH solution in a non-alcoholic medium. Yields of the alcoholic process and total non-alcoholic yield related to stoichiometric yield with 100% pure aluminum.

	Hydrogen 100 ml solution (l)	HydrogenEnd of process (l)	Hydrogen Total (l)	$\eta_{process}$ (%)	η_{total} (%)
Pure aluminum A4	30,5	38,9	38,9	99,7	99,7
Automotive aluminum A2	21,8	32,2	34,6	82,6	88,7

Aeronautical aluminum A3	20,8	29,9	33,3	76,7	85,4

7.5. Purity of hydrogen

The purity of the hydrogen obtained has been analyzed, just in case that the aluminum wastes could contain any volatile or reactive elements that could generate some undesirable gas. No CO, C_1-C_6 hydrocarbons, or C_1-C_3 oxygenate compounds have been detected in the gas micro chromatograph. No alkali has been detected by pH analysis. Hydrogen purity is greater than 98% in all cases, with impurities in the air (<0.06%), alcohol (<0.007%), and water (> 1.28%). This is due to the lack of tightness of the system connections since it is made in glass, which allows the air to pass through the circuit, and the use of a water filter that generates more moisture than the dryer can absorb. The alcohol obtained after condensation and filtration, for hydrogen flow rates lower than 3 l/min, is negligible (<0.007%), but a perfect design of the condenser as a function of the flow rate is extremely important.

7.6. Purity of aluminum hydroxide

The purity of the aluminum hydroxide obtained from the sodium tetrahydroxyaluminate resulting from the reaction after filtration was finally analyzed. First, it is easy to isolate the alcohol from the aluminate solution. It can be carried out by decantation due to the lower density of the alcohol, or by its extinction in the oven due to evaporation. Concerning the aluminate solution, it is always together with unreacted solid aluminum particles or their alloying elements, which must be separated by porous filters. Then it is necessary to reduce its pH and start crystalizing the aluminum hydroxide. After the crystallization, washing is carried out [26], finally being introduced into an oven at 1000°C to get the aluminum oxide.

From the results obtained in *Table 9*, it was seen that the content of aluminum in aluminum oxide was higher in aluminum waste from the automotive industry than in those from the aeronautical industry. The content of zinc in the alloy damages its purity due to the appearance of zinc oxides [27]. Silicon also brings impurities to the hydroxide, but far less than the previous ones. It would be necessary to generate hydrogen from low-zinc aluminum products or eliminate such impurities in the aluminum in the final product.

Table 9. Analysis of the purity of aluminum oxide obtained.

Type of aluminum	Initial impurities (%) Cu – Zn – Fe - Si	Final impurities (%) Cu – Zn – Fe - Si	Content Al (%)
A4 (pure)	< 0,05	<0,01	24,4
A2 (automotive)	1,5 – 0,7 – 0,5 - 5	<0,01-0,11-0,02-0,19	24,3
A3 (aeronautical)	1 – 5 – 0,2 – 0,5	<0,01-0,75-0-0,04	23,2

7.7. Economic Study

When studying whether this system is profitable, it is usually done from an energy point of view, assuming that aluminum is manufactured only to generate hydrogen and not as waste, so it is not viable [28], in this section, it is studied from the point of view from an economic point of view.

The price of the aluminum machining chips [~ 0,6 \$/kg (LME 2020)] is low, and it could be used for green hydrogen production [29], as you can see in Table 1. 9 kg of aluminum are needed to obtain 1 kg of hydrogen, so the cost would be 5.4 \$ / kg H2. But the residue obtained is 3.7kg Al_2O_3 whose cost is [~ 0.3 \$ / kg Al_2O_3 (LME 2020)] so the final cost, without considering the operating costs of 10%, would be 4.3 \$ / kg H2.

Table 10. Cost of aluminum green hydrogen.

Price Aluminium breakage scrap	Price Al$_2$O$_3$	Cost/kg hydrogen (9 kg Al)	Sale Al$_2$O$_3$ (3,7kgAl$_2$O$_3$/kg Al)	Cost/kg hydrogen Total
0,6 $/kg Al	0,3 $/kg Al$_2O_3$	5,4 $/kg H$_2$	1,1 $/kg H$_2$	4,3 $/kg H$_2$

8. Conclusions

The main conclusion drawn from this research is the possibility of obtaining high purity green hydrogen from aluminum wastes in a controlled manner by dosing the 7.5M NaOH solution in an alcoholic medium with isopropyl alcohol, and this system is economically profitable.

The active aluminum surface is enough to may work as a function of the water flow (contained in the NaOH solution) only, to obtain the desired hydrogen flow rate continuously. The theoretically required surface to ensure an average hydrogen flow rate of 1 liter/minute has been estimated at 220 mm^2 approximately. The theoretical formulas for calculating the active surface and the hydrogen flow rate to be obtained, have been studied, knowing that the addition of alcohol will decrease the yield, which has not been analyzed in this article. If the aluminum is recycled, it would be convenient to grind it in granular form and evaluate its impurities. Different aluminum wastes from the industry after a machining process have been tested. Those used in workshops and the automotive industry perform better than those used in the aeronautical industry, although in both cases the hydrogen obtained is more than 80% of the theoretically expected hydrogen. The purity of the hydrogen obtained is high. Its main impurity is moisture, and no element could affect the durability of the fuel cell, but in any case, a filter should be placed to eliminate escaping alcohol vapors from the condenser, and an excellent purging and connection should be done to prevent the entrance of air from the outside.

It has also been concluded that an almost constant hydrogen flow rate can be achieved by this method, regardless of the amount of aluminum in the reactor, by controlled dosing of NaOH solution in an alcoholic medium, also controlling the refrigeration and filtration of the sodium hydroxide particles. Finally, the derived sodium hydroxide obtained has zinc and some silicon impurities, so aluminum wastes from the automotive industry are preferred to those from the aeronautical industry. In any case, such impurities should be eliminated in the treatment of the final derived products to be able to commercialize them. With this analysis an important contribution to the metal aluminum wastes valorization has been performed and developed, giving a second life to this type of wastes. This process could be used for metal industries that produce, yearly, tones of metal aluminum wastes, for instance, car industry or aerospace industry, but other industries like metal recovery plants or industries which work with metal aluminum can be interested in the described study-analysis.

So finally, as a main conclusion, the determines that it is possible to obtain green hydrogen from aluminum at a lower price or like other methods by choosing the appropriate machining waste, evaluating sectors like automotive or aerospace, where it is possible to obtain better performance. Likewise, a model is developed to determine the amount of hydrogen obtained as a function of the chip geometry and the dissolution temperature.

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