Technology

Sustainable and renewable hydrogen production from recycled aluminum

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ABSTRACT

The whole world has been suffering strong consequences related to climate change. The intense use of fossil fuels in the chemical and automotive industries have put the environment in jeopardy. Thus, the industry has achieved a point of no return and it is urgent the development of renewable and sustainable technologies. Hydrogen has been pointed as a key component of the new era in industry since it can be produced in a clean and sustainable way. Currently the development of hydrogen fuel cells technology has put the automotive sector ahead of the chemical industries in relation to studies regarding the hydrogen production. Chemical industries produce hydrogen with technologies reliant on fossil fuels while the automotive sector has been looking for renewable forms of hydrogen generation. Trains powered by hydrogen fuel cells are a reality in Europe, for instance. Hydrogen generation technological advances must match the pace of the development of fuel cells electrical vehicles in order to the environmental goals and widespread application of fuel cell systems to be achieved. The present study addresses the hydrogen generation from the spontaneous reaction between aluminum and aqueous solution of sodium hydroxide. Aluminum is a metal that presents high exergetic value and can be recycled several times without losing its thermo-mechanical properties. That makes the use of aluminum especially appealing. It will make hydrogen generation a cleaner and more affordable process. Our findings demonstrate that it is possible to predict the kinetic behavior of the reaction using data obtained by the conductometric method. Graphs of electrical conductivity vs time show that is possible to verify the order of the reaction. We will present concepts of kinetic, thermodynamic and transport phenomena of the reaction between solid recycled aluminum and sodium hydroxide in an aqueous solution. The knowledge acquired throughout this study will contribute to the development of a new reactor and as a consequence, a new renewable and sustainable industrial system of hydrogen generation.

Keywords: Reactor; Aluminum; Sodium hydroxide; Sodium Aluminate; Hydrogen.

NOMENCLATURE

The nomenclature section should list, in alphabetical order, all used symbols, their definitions and their unit, in alphabetical order, as in the examples below:

Ci	molal concentration of species i, mol/kg
Cpi	specific heat of species i, J mol-1 K-1
Ea	activation energy, kJ mol-1
H0	standard enthalpy at 298,15K, kJ mol-1
G0	standard Gibbs free energy at 298,15K, kJ mol-1
kapp	constant pre-exponential factor, mol s-1 m-2
k	constant of reaction, mol s-1 m-2
ks	constant of reaction related to the kinetics
kc	constant of reaction related to the mass transfer rate
Ke	equilibrium constant of the reaction, dimensionless
r	reaction rate, mol s-1
L	thickness of flat plate, mm
M	molar mass, kg kmol-1
N	mol number, mol
Ni0	initial mols of species i, mol
R	ideal gas constant, 8,314 kJ mol-1 K-1
S	superficial área, mm2
t	time, s
T	temperature, K
wt	weight(mass), %
XEB	adiabatic conversion (dimensionless)
XE	equilibrium conversion (dimensionless)
X	reaction conversion (dimensionless)

Greek symbols

ρAl	Al molar density, mol dm-3
τ	time to complete de reaction, s
Δ	variation
ϴ	ratio

Subscripts

aq	aqueous solution
g	gas phase
i	species type(reagents/reactants)
l	liquid phase
pro	products
R	reaction
s	solid phase
rec	reactants

1. METHODOLOGY

The industrial generation of hydrogen consumes a large amount of fossil fuels such as naphtha and natural gas through a process called steam reform. Steam reform is currently the most widely used process for large-scale hydrogen generation. Water electrolysis is another well-known method used, although the high costs of installation and maintenance are aspects that make this method less used than steam reforming. (Holladay et. al, 2009; Rostrup-Nielsen, 2005; Wang et. al., 2009; Wang et. al., 2014). There is an increase of the number of studies related not only to water electrolysis in order to make it more attractive from a financial point of view (Wang et. al., 2014) but also regarding to alternative forms of energy with the potential to be used in hydrogen generation, such as wind energy, solar energy or even green hydrogen production processes (Mosca, 2017; Nikolaidis and Poullikkas, 2017). In addition to the methods mentioned above, there is another relevant industrial method, but less used than steam reforming, called partial oxidation (gasification) (Holladay, 2009; Nikolaidis and Poullikkas, 2017). A comparison among the different hydrogen production methods can be made from an energy and an economic viewpoint (Holladay, 2009; Nikolaidis and Poullikkas, 2017 and Luo, 2018). Such studies, at this time of the industrial era has been guiding researchers that aim their efforts to produce hydrogen in an affordable, renewable and sustainable way.

Other examples of the use of hydrogen in industry are the production of ammonia and the subsequent production of nitrogen fertilizers (urea), the production of hydrogen peroxide and the hydrogenation used in the food industry. The chemical industry urgently needs alternative forms of hydrogen generation on a large scale, since it will continue to use hydrogen in its formulations.

Automotive industry is intensely using hydrogen. The automotive industry is undoubtedly at the forefront of the search for alternatives that make transportation independent of fossil fuels, such as electric or fuel cell-powered vehicles. The automotive industry is also researching hydrogen generation from aluminum for use in fuel cells (Soler, 2007).

The major conundrums associated with the use of hydrogen in vehicles are the difficulty of fuel distribution, as cities and countries that do not have the adequate distribution network and would have high expenses related to the installation of generation plants for an entire infrastructure and large-scale hydrogen storage. Obviously, security-related issues make installing a distribution network more expensive. Large chemical industries are centralized, while a hydrogen distribution network for vehicles would require hydrogen generation to be decentralized, so that remote locations would also be able to make available the amount of hydrogen needed to match the vehicles demand (Rostrup-Nielsen, 2005).

It is in this sense that other alternative technologies are being studied and developed. It is very important to emphasize that the knowledge acquired from the chemical industry is extremely useful for the new information era and the industry of the future. In this way, the hydrogen production from aluminum (Wang et. al., 2009 Alessandrov et. al., 2003; Belitskus, 1970, Liu et. al., 2018; Parmuzina and Kravchenko, 2008; Soler et. al., 2009; Soler et. al., 2009), especially methods using recycled aluminum (Hiraki and Akiyama, 2009; Hiraki et. al., 2005 and Hirake et. al., 2007), have been extensively studied and very useful discoveries have been brought to light so that developments carried out in the laboratory can be transformed into a viable chemical processes to produce hydrogen on a large scale in a sustainable way.

The present study uses small squared pieces of an aluminum-silicon alloy, with a high degree of purity (99.09%), obtained mainly from sources that recycles wasted aluminum, so that a more accurate analysis of the kinetics of the reaction can be performed. Metallic aluminum has thermodynamically high chemical exergy, of (788.61±0.5) kJ/kg, which makes recycled aluminum extremely attractive for further developments of the chemical process (Hiraki and Akiyama, 2009). In addition, it is known that approximately one kilogram of pure aluminum can be used to produce between 2.22 kWh to 4 kWh of energy in the form of hydrogen (Soler et. al., 2009 and Zhuk et.al., 2006). Another remarkable factor is that aluminum can be recycled many times, without losing its thermo-mechanical properties. Furthermore, it is relevant to take in consideration that the cost of obtaining recycled aluminum is less than 10% of the total cost of aluminum production from bauxite. Thus, there is a trend of technological development of a new hydrogen generation process considering the use of recycled aluminum ((Hiraki and Akiyama, 2009; Hiraki et. al., 2005 and Hirake et. al., 2007).

The main objectives of this paper are to prove in laboratory scale the kinetics of the reaction for hydrogen production from the spontaneous reaction between solid aluminum and an aqueous solution of sodium hydroxide and to find the order of the reaction in relation to the reactants. To achieve the aforementioned objectives, the degree of isothermality of the reactor on a laboratory scale must be taken into account so that the data obtained in the reaction system can be reliable. Studies were carried out to analyze mainly the reaction order (and consequently the conversion) and the feasibility of hydrogen production. The method to be used so that the reaction can be accurately observed is called conductometric method, in which the electrical conductivity of a solution containing electrolytes can be measured and provide reliable results, which after mathematical treatment it can provide molal concentration values (mol/kg) of the products and indicate the order of reaction. If the reaction system has electrolytes in solution, electrical conductivity can be measured as a function of time. When there is no more variation in the electrical conductivity of the solution, this is a strong indication that the reaction has reached the thermodynamic equilibrium or even has effectively ended.

2. THERMAL KINETIC ANALYSIS

In order to be considered for the design of a chemical reactor, the Eq. (1) must not only be considered kinetically favorable, but also thermodynamically feasible. The Eq. (2) shows that not only the sodium hydroxide but also the aluminum can be recovered in the process.

$$\mathrm{Al}_{(s)} + \mathrm{NaOH}_{(aq)} + 3\mathrm{H_2}O_{(l)} \rightarrow \mathrm{Na[Al(OH)_4]}_{(aq)} + 3/2\mathrm{H}_{2(g)} \qquad (1)$$

$$\mathrm{Na[Al(OH)_4]}_{(aq)} \rightleftharpoons \mathrm{Al(OH)}_{3(s)} + \mathrm{NaOH}_{(aq)} \qquad (2)$$

Several calorimetry data were obtained from the literature in order to initially predict the thermodynamic behavior of the Eq. (1). The specific heat, enthalpies and Gibbs free energy were obtained from values available in the literature (Chen et. al., 1991; Chen et. al., 1994 and Magalhães et. al., 2002). Chen et. al. (1991) were the first to obtain thermodynamic data of aqueous sodium aluminate solution from a reaction systems involving aqueous solution of NaOH and solid aluminum. Thus, the following results were obtained: $\Delta H_R{}^0 = -(416.2 \pm 0.7)$ kJ/mol obtained with Eq. (3) and similar calculation was made to obtain the Standard Gibbs Free Energy of the reaction, $\Delta G^0 = -(436.56 \pm 0.5)$ kJ/mol. With the Eq. (4), it is possible to determine the equilibrium constant $K_e = 3.063\mathrm{x}10^{76}$.

Below there are some equations related to the energy balance:

$$\Delta H_R^0(T) = \Sigma H_{pro}^0 - \Sigma H_{rec}^0 \quad \text{(Standard Entalpy of reaction)} \qquad (3)$$

$$\Delta G^0 = -RT \ln K_e \qquad (4)$$

The evaluation of the behavior of the equilibrium constant as the reaction progresses, is given by the Van’t Hoff law applied to the system which yields:

$$\frac{d \ln K_e}{dT} = -\frac{\Delta H_R{}^0}{RT} \qquad (5)$$

$$\Theta_i = \frac{N_i{}^0}{N_{NaOH}{}^0} \qquad (6)$$

For a full understanding of the reaction, undoubtedly it is necessary to master the energy balance of the reaction and to analyze the behavior of the reaction regarding the conversion when the temperature increases, keeping in mind the strong exothermic behavior of the reaction. This can be understood by the adiabatic conversion X_{EB}, Eq. (7). It demonstrates how the temperature increases until the end of the reaction and gives important information about how the temperature can be controlled so the maximum conversion is achieved.

$$X_{EB} = \Sigma \frac{\Theta_i C_{pi}(T - T_0)}{\Delta H_R{}^0} \qquad (7)$$

With these three thermodynamic parameters known ($\Delta H_R{}^0$, ΔG^0 and K_e), it can be identified that the reaction is highly exothermic, spontaneous under standard conditions and that the thermodynamic equilibrium is achieved quickly because the magnitude order of the equilibrium constant of the Eq. (1) is extremely high (10^{76}). This is an important result to be considered before any experimental test to be performed. The researcher conducting the experiment is now aware that the reaction occurs quickly and with great release of energy. We emphasize that the Eq. (1) is not a reaction at chemical equilibrium since it runs in only one way. However, it will tend to reach the thermodynamic equilibrium. The equilibrium constant indicates the behavior of the conversion as the temperature increases. That is an important parameter to show how quickly the reaction reaches the equilibrium.

The practical studies for obtaining the activation energy were conducted in sodium hydroxide solutions of 2.0 and 2.5 mol/kg. The theoretical graphs of how the equilibrium constant, as well as the adiabatic conversion vary, are presented in Fig. 1 e 2 (using only 2.5 mol/kg data). Comparing the Fig.1 e 2, it is possible to observe that the maximum conversion of the system in an adiabatic reactor is 50%considering if there is the crossing point between the line for adiabatic conversion and the curve for equilibrium constant. For an exothermic reaction it is known that the total conversion (X) decreases when the temperature increases. From the Fig. 2 it is possible to observe how sharp is the decrease of the equilibrium constant while the temperature of the reaction increases. A detailed study of Fig. 1 and 2 and the obtained conclusions of the kinetics of the reaction are the first steps toward the design of an industrial reactor for this current study. A more in depth study of how heat transfer influences the conversion (X) of the Eq. (1) is the object of ongoing studies related to hydrogen generation based on the reaction of $Al_{(s)}$ and $NaOH_{(aq)}$.

As we progress in the study, there is the impression of being in uncharted waters. The reactional solution is composed by a strongly heterogeneous solution, which has solid, liquid and gaseous phases with presence of dissolved electrolytes as well. That is why it is so important to choose the accurate thermodynamic model to evaluate the properties of the solution during the chemical reaction. Pitzer's thermodynamic model (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974, Pitzer and Kim, 1974 and Pitzer, 1980) can be used to obtain the activity coefficient in diluted aqueous solutions of NaOH/ $Na[Al(OH)_4]$ and thus, to present the thermodynamic behavior of the solution and a better understanding of the Eq. (2) (Königsberger et. al., 2006). It is known that the Pitzer model takes into account short-range and long-range forces (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974, Pitzer and Kim, 1974 and Pitzer, 1980), but there is a peculiarity in the reaction system under study that was brilliantly clarified by the Non-Random Two Liquid (NRTL) electrolytic thermodynamic model (Chen and Evans, 1986; Song and Chen, 2009). In the electrolytic NRTL model, long and short-range forces are also taken into account, as well as three different types of interactions that occur in the reaction Eqs. (1) and (2), namely:

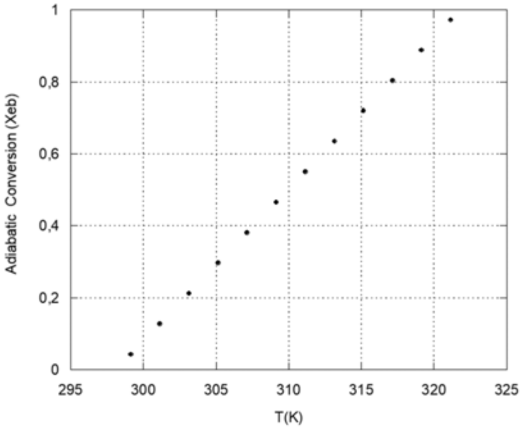

Fig. 1 – Influence of the Temperature on the Adiabatic Conversion (considering a solution of 2.5mol/kg).

i) interactions between cations surrounded by anions and gas molecules; ii) interactions between anions surrounded by cations and gas molecules and iii) interactions between gas molecules surrounded by cations and anions. This approach makes the system thermodynamically understood (Chen, 1986 and Song and Chen, 2009). The results of the electrolytic NRTL model in obtaining the activity coefficient and a detailed thermodynamic study of the behavior of the Eq. (1) in relation to temperature will provide sufficient information to predict whether or not the reaction is thermodynamically feasible at the industrial level.

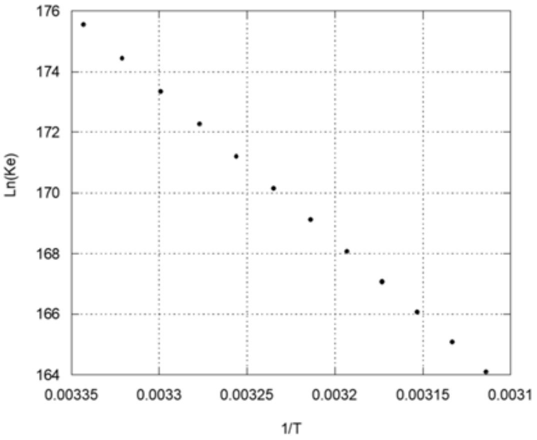

Fig. 2 - Influence of the Inverse Temperature on the Logarithm Neperian (of the Equilibrium Constant)

i) interactions between cations surrounded by anions and gas molecules; ii) interactions between anions surrounded by cations and gas molecules and iii) interactions between gas molecules surrounded by cations and anions. This approach makes the system thermodynamically understood (Chen, 1986 and Song and Chen, 2009). The results of the electrolytic NRTL model in obtaining the activity coefficient and a detailed thermodynamic study of the behavior of the Eq. (1) in relation to temperature will provide sufficient information to predict whether or not the reaction is thermodynamically feasible at the industrial level.

The study of the thermal behavior of the reaction system is paramount and some information has already been obtained (Li et. al., 2014). As mentioned before, the behavior of the aluminate ions in the solution is what will define the success in the recovery of the aqueous solution of sodium hydroxide and aluminum. The structure of aluminate ions in solution is among the most important problems of aluminum chemistry (Eremin et. al., 1974; Radnai et. al., 1998 and Tossell 1999).

Results from viscous studies (Sipos er. Al., 2001) and density studies (Königsberger, et. al, 2005 and Reynolds, 2006) has been used to understand the behavior of the aluminate solution from the fluid mechanics point of view. For the present investigation, the authors considered studies performed about the density of sodium aluminate solutions and the influence of the temperature on the density of the electrolyte solutions and decided to use mol/kg as the concentration unit. Then the concentration values were recorded on a molal basis because when working with electrolyte solutions and using this concentration unit, there is an advantage since the molality is independent of the temperature variations. That does not occur with the molarity, which is dependent on the density of the solution which is directly related to temperature variations (Prausnitz et. al., 1999).

The main objective of the current study, as aforementioned is prove the order of the reaction described by the Eq. (1). The chemical reaction between solid aluminum and the sodium hydroxide aqueous solution is heterogeneous and non-catalytic, with strong presence of electrolytes in solution which one influence directly the hydrogen production. From other studies is it known that high concentrations of aluminate ions is a hindrance for the hydrogen production (Aleksandrov et. al., 2003). The combination of intrinsic phenomenon of the reactive system, such as the heat and mass transfer are taken into account, as well as the particular characteristics of the kinetics of the reaction between a solid phase and a liquid/aqueous phase, which generates a large amount of electrolyte and hydrogen.

The sequence of steps taking place when a component of a fluid reacts with a solid is similar to that followed by a fluid-solid reaction of the catalytic type.

The reaction at an active center of the solid must occur by adsorption of the reagent fluid at that active center followed by a surface reaction in which the adsorbed molecule participates. Such reactions are also known as topochemical reactions. It is really important to emphasize the fact that the rate of reaction regarding a solid phase may be determined by the available surface area S of the solid particles (Upadhayay, 2006). This implies that particles of solid aluminum must have regular geometric shape so that the effects of all variations of concentration in the solution regarding sodium hydroxide can be observed accurately. For an irreversible reaction, the rate (velocity) of the reaction is determined by the following four step (Levenspiel, 1999):

- Mass transfer of the global fluid to the external surface of the particle;
- Intergranular diffusion in a particle (each small flat plate);
- Adsorption in the active center of the solid reactants;
- Intrinsic reaction in the active center.
- Mass transfer of the products from the active center to the fluid (solution).

The main focus of this study is the reaction shown in the Eq. (1). The reaction represented by the Eq. (2) is also relevant because it is from that reaction that it will be possible to develop a continuous, renewable and sustainable process of hydrogen generation and recovery of all reactants, such as solid aluminum and sodium hydroxide solution. The Eq. (2) is directly involved with the word "sustainability", because it is known to the scientific and industrial environment that it occurs in the aluminum production from bauxite, in a chemical process known as Bayer process (Königsberger, et. al, 2006).

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The transformation of aluminum hydroxide by Bayer process into alumina and then the obtention of pure aluminum by Hall-Heróult electrolysis makes a new process of hydrogen generation non-sustainable due to the high consume of electricity and maintenance by the Hall-Heróult electrolysis. Even though the renewable and sustainable approach related to the Eq. (2) is not part of the scope of this current study, it should be part of further investigation so that the hydrogen generation process represented by Eq. (1) could become a reality implemented in industrial plants. The Fig. 3 shows a representation of the system under study.

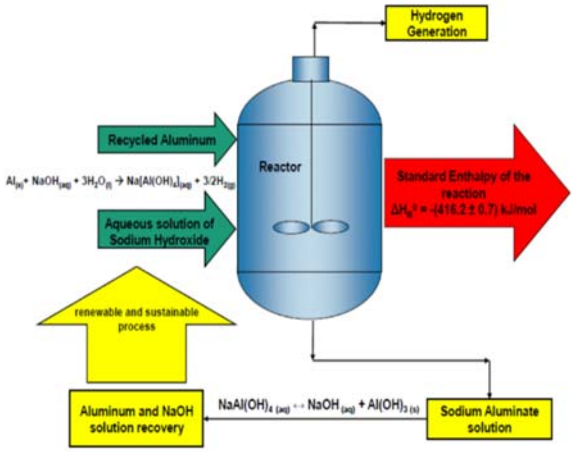


Fig. 3 – Representation of the hydrogen generation system

Several studies have been carried out about the kinetics of the Eq. (1) in order to prove the order of the reaction (Wang et. al., 2009; Alesandrov et. al., 2003; Belitskus, 1970; Liu et. al., 2018; Parmuzina and Kravchenko, 2008; Soler et. al., 2009; Soler et. al., 2009, Hiraki and Akiyama, 2009,Hiraki et. al., 2005 and Hiraki et. al., 2007), as well as how much hydrogen can be produced using volumetric methods. Such studies have provided essential and valuable data that has supported this investigation. Although hydrogen generation is the main scientific contribution of the authors, it is paramount for completeness of the investigation to have the understanding the behavior of the reaction in an electrolyte solution, which we will perform and discuss in the following paragraphs. The conductometric method will demonstrate the consumption of the reagents and consequently the formation of the products.

The dissolution of NaOH into water produces OH^- ions, inhibiting the formation of an oxide layer on the aluminum surface, thus eliminating passivation and allowing the metallic aluminum to react and to produce hydrogen. An important remark is that the reaction between metallic aluminum and NaOH in an aqueous solution occurs spontaneously at temperatures of 25 °C (Wang et. at., 2009, Parmuzina and Kravchenko, 2008; Soler et. al., 2009; Soler et. al., 2009). The Pourbaix diagram predicts that in aqueous solutions with strongly basic pH, the Al^{+3} ions will generate the aluminate ions ($Al(OH)_4^-$), as shown in the Eq. (1). It also predicts that as the concentration of the solution increases, there is a decrease of the pH value and the consequent formation of other undesirable ions in the solution. That result was also confirmed by the scientific community (Eremin et. al., 1974; Radnai et. at., 1998, Tossell, 1999, Hovey et.al., 1988; Moolenaar et.al., 1970). Therefore, experiments in laboratory for the development of a reactor should consider aqueous solutions of sodium hydroxide of low concentration to maintain the pH value in a range that favors the formation of aluminate ions. The main reason to consider diluted solutions is that the same aluminate ions if in high concentrations can inhibit the production of hydrogen [9]. The point of equilibrium between the concentration and formation of aluminate ions must be determined. The system should produce hydrogen in a level such that the aluminate solution should be renewable in order to be feasible to recover aluminum and sodium hydroxide. The aluminate ions should not be a hindrance for hydrogen molecules formation.

The theory of Shrinking Core Model for non-catalytic chemical reactions between solids and liquids (aqueous phase) can explain in detail the way as the solid particles of aluminum are to be consumed during the development of the reaction [39]. The Shrinking core model has recently been studied and applied to the Eq. (1), considering solid squared particles of pure aluminum obtained from recycling process for this material. The aluminum-silicon alloy used in the herein study will show the importance of using recycled aluminum sources. It is possible to study Eq. (1) using a Shrinking core model for a reaction between a solid phase and a fluid phase (Hiraki et. al., 2005). The details of the mathematical model that represents this type of reaction will be presented later in the section 4.

3. METHODOLOGY

The aqueous solutions were prepared using distilled water and pearly sodium hydroxide (NaOH, CAS 1310-73-2) with a purity of 99.5%. Recycled aluminum (aluminum-silicon alloy 1050 ABNT/ASTM) was used according to the composition shown in the Table 1. The aluminum was cut into small squared flat pieces of 0.5 cm^2 (superficial area) and 0.2 mm thick, in order to keep the geometry as homogeneous as possible among the solid aluminum particles. Regular laboratory glassware was used, such as beakers, pipettes, glass rod and Erlenmeyer. Others instruments used were Agitator Fisatom (mod710, serie 1955122, 230V, 60Hz, 25W, 150rpm), Chemical Thermometer Incoterm 1°C (360°C - Cod5008), EC700 Benchtop Conductivity Meter, 2301T-F Conductivity electrode and Electronic balance.

Table 1 – Aluminum 1050 ABNT/ASTM

Element	Composition(wt%)
Al	99.09
Si	0.25
Fe	0.40
Cu	0.05
Mn	0.05
Mg	0.05
Zn	0.05
Ti	0.03
Others	0.03

3.1. Procedure

The conductometric method used to determine the kinetics of the chemical reaction between an aqueous solution of sodium hydroxide and the solid aluminum. This method was chosen because it gives the understanding of the kinetic behavior of the reaction instead of only measuring the volume of hydrogen produced, although it is necessary to understand that for practical industrial purposes. The products of the reaction between a hydroxide and solid aluminum generate a huge number of ions that increases the electrical conductivity of the solution. Thus, the measurement of the electrical conductivity of an electrolyte solution is one of the most used methodologies to quantify the products of an ionic chemical reaction. Therefore, it is a quantitative method. In order to obtain reliable data, there was a concern about keeping some variables constant, such as temperature and pH. This was taken into account since the electrical conductivity of the solution can be measured in relation to the time of the reaction. We emphasize that the chemical reaction between solid aluminum and aqueous sodium hydroxide solution is extremely exothermic and for safety reasons, all the reactions were carried out with dilute aqueous solutions of NaOH. Although temperature (T) and pH were kept constant during all tests, T, pH and electrical conductivity were monitored over time. According to the stoichiometry of the Eq. (1), it is possible to identify that initially there will be H_3O^+ ions, hydroxyl ions(OH^-), aluminum ions (Al^{+3}) and sodium ions (Na^+). As the reaction begins, there is also the formation of aluminate ions ($Al(OH)_4^-$) and H_2 molecules. The presence of electrolytes in solution is the key point for the conductometric method to be used. In the procedures, chemical reactions were conducted respecting the stoichiometric quantities of the reactants, but in relation to the reaction volume and the quantity of reagents, a scale of 1:10 was used. If we had used the 1:1 scale, there would be too much gas being generated in the reaction system and the gas would act as an insulator, making the electrical conductivity measurements to become unreliable. On a small scale and with diluted solutions, it is possible to conduct the tests with the presence of hydrogen causing not significant interference in the electrical conductivity readings. Regarding the ions in the reaction solutions, we observed that there is a strong presence of aluminate ions in solution. As the reaction takes place, the solution becomes more concentrated and other ions will be formed, as described previously.

Although the chemical Eq. (1) is spontaneous, in order to homogenize the solution, slight agitation (≤ 150 rpm) was maintained as already indicated in the literature [9] to avoid the decanting of the aluminum particles.

The reactions were run between squared pieces (flat plates) of solid aluminum of 0,5 cm^2 of superficial area and 0,2 mm of thickness and a diluted aqueous solutions of sodium hydroxide.

During tests four types of dilute aqueous sodium hydroxide solutions were studied, namely: 0,25 mol/kg, 0,5 mol/kg, 0,75 mol/kg and 1,0 mol/kg respectively.

As previously mentioned, the stoichiometric quantities of the reactants were respected, in a 1:10 scale. Tests were performed for each concentration and the average values used to show the results measured in the three runs of each concentration. Bulk quantities were weighed on an electronic scale and volume quantities (water) were measured using pipettes and beakers. The method indicates the thermodynamic equilibrium of the reaction when there are no more changes in the electrical conductivity (the chemical reaction reaches a plateau). The values measured in μS/cm (electrical conductivity) can be converted in ppm (640 scale) and then in molal concentration (mol/kg) of products. With the concentration data and some mathematical treatment, it is possible to obtain the order of the reaction, as demonstrated later in the text. Another important observation is the fact that there is an amount of water used to prepare the aqueous solutions and, according to the Eq. (1), there is an amount of water that is part of the reactants. From the aqueous solutions, it is known that H_3O^+ and OH^- ions are formed and they influence the amount of electrolytes in the solution. However, in reactions in which the order and the molecularity are not the same, due to one of the reactants to be in excess, such reactions are called pseudo-order reactions. Thus, the rate of the reaction has no dependency regarding the water concentration since water is the solvent that is in excess. The order and the concentration of water is considered 1 and it does not appear on the rate of the reaction. The rate is only function of the superficial area of the aluminum particles and the concentration of NaOH solution. That is important because the conductometric method gives answers about Al and NaOH consumption and how the amount of water is directly related to the reaction has been given only by the mass balance of the reaction.

The procedure for obtaining the activation energy of the Eq. (1) was carried out in aqueous solutions of 2.0 mol/kg and 2.5 mol/kg also on a 1:10 scale. For concentrations above 1 mol/kg, the reaction becomes unsafe due to the release of a huge amount of heat. Three reactions were done for each concentration and in these cases, the variation of temperature was measured over time.

4. MATHEMATICAL MODEL

The mathematical model developed in this study took into consideration the following: i) the mass conservation laws, ii) energy conservation laws and iii) the kinetic of the reaction in a semi-batch reactor.

The Eqs. (8), (9), (10) are the rate laws which show the consumption of reactants and the formation of products as a function of time.

$$-r_{NaOH} = \frac{dC_{NaOH}}{dt} \tag{8}$$

$$r_{Na[Al(OH)4]} = \frac{dC_{Na[Al(OH)4]}}{d} \tag{9}$$

$$r_{H2} = \frac{dC_{H2}}{dt} \tag{10}$$

where C represents the concentration of the different species in the solution.

Inside the small reactor there are solid, liquid, gas phases and the electrolytes in solution which gives important information about the reaction. The Eq. (11) shows the relation among the rate laws of reactants and products.

$$-r_{NaOH} = r_{Na[Al(OH)4]} = \left(\frac{2r_{H2}}{3}\right) \tag{11}$$

The kinetic of the reaction between solid aluminum and an aqueous solution of sodium hydroxide is represented by the Eqs. (12) and (13), (Updhyay, 2006). The solid phase is represented in the Eq. (12) by the superficial area S.

$$r_{NaOH} = k_{app} S[OH]^- e^{-Ea/RT} \tag{12}$$

$$k = k_{app}.e^{-Ea/RT},\ [mol/s.m^2] \tag{13}$$

From the Eq. (13) we can obtain the constant of the reaction. Our goal is to demonstrate that the Eq. (12) represents properly the behavior of the reaction between aluminum and sodium hydroxide.

From the Arrhenius law represented by the equation (13) and the equation (14), it was possible to obtain the activation energy of the reaction (E_a) and the pre-exponential factor (k_{app}). The rate law was not applied to the Aluminum because there is no meaning to represent the concentration of solid state in the reaction. Shrinking-core can be used to determine how the aluminum influences the reaction.

$$\frac{\ln k_1}{\ln k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{14}$$

The Van't Hoff law represented by Eq. (5) shows how the equilibrium constant of the reaction K_e decreases for an exothermic reaction while the temperature increases. In this study, the effect of the temperature on the reaction is to be investigated only by using mathematical relations. The experiments were conducted to evaluate the hydrogen generation and to prove the kinetic for a diluted aqueous solution of sodium hydroxide.

The mathematical model using the Shrinking core model is able to represent the main aspects of the consumption of recycled solid aluminum particles as the reaction occurs with the sodium hydroxide solution.

The total conversion of the reaction (X) for squared aluminum is dependent on the thickness of each particle and is represented by the Eq. (15), (Levenspiel, 1999), where L is the thickness of each particle.

$$X = 1 - \frac{1}{L} \tag{15}$$

The rate of the reaction of a system containing a solid depends directly on the surface area of the particles, as well as on the variation in the concentration (and consequently the number of moles) of the reactants. According to the Eq. (16) the number of mols of aluminum is represented by the relation between the molar density and molar mass of the aluminum.

$$-\frac{d}{dt}\left(S.L.\frac{\rho_{Al}}{M_{Al}}\right) = S\frac{dN_{Al}}{dt} \tag{16}$$

The rate at which the reactants are consumed depends on the reaction constants which represents the kinetics and mass transfer on the surface of the solid particles. That is expressed by the Eq. (17), where k_s is the constant related to the kinetics of the reaction and k_c is the constant referring to the mass transfer rate.

$$\frac{dN_{Al}}{dt} = \frac{-C_{NaOH}}{1/k_s + 1/k_c} \tag{17}$$

Using the Eqs. (16) and (17) and solving then for dL/dt we obtain

$$\frac{dL}{dt} = \frac{C_{NaOH}.M_{Al}}{\rho_{Al}.(1/k_s + 1/k_c)} \tag{18}$$

Using the method of separation of variables and performing the integration of the Eq. (19) and Eq. (20) we obtained the time required for the total reaction to occur (conversion X). For sake of completeness, it is necessary to perform a thermodynamic analysis to find the optimum reaction temperature and find out the time needed to achieve this particular conversion.

$$\frac{\rho_{Al}}{k_s.C_{NaOH}.M_{Al}}\int_0^L dL = \int_0^\tau dt \tag{19}$$

$$\tau = \frac{\rho_{Al}.L}{k_s.C_{NaOH}.M_{Al}} \tag{20}$$

5. EXPERIMENTAL SET UP

The Fig. 4 shows the set up used to generate the experimental results. A 2301T-F conductivity electrode was connected to the conductivity meter and it was possible to measure the electrical conductivity during the experiment. All the values of the electrical conductivity and temperature were read on the display of the conductivity meter. In the center of the Fig. 4 we see the Agitator Fisatom and a beaker where a small reactor can be simulated. During the tests a beaker and an Erlenmeyer were used as a reactor. The Erlenmeyer is more appropriated than a beaker because the volume of hydrogen can be measured when connecting the Erlenmeyer to a flow meter. The speed of the agitator can be regulated through a black button located on the top of the equipment. During the tests the speed was kept in 150 rpm with is just speed to avoid the decanting of the aluminum pieces.

Inside the Erlenmeyer there is the thermometer used to get the activation energy. We can observe the recipient with solid sodium hydroxide and some squared pieces of solid recycled aluminum on the table.

6. EXPERIMENTS

From the conductometric method the following experimental results of electrical conductivity vs time are given in the Fig. (5)-(12), for different concentration of electrolyte:

Tests with three chemical reactions were conducted for each value of molal concentration. The average of the values of electrical conductivity was obtained and the Fig. 5, 6, 7 and 8 were plotted. The data were collected during the first 20 minutes of each reaction. This fact is notorious, because after 20 minutes, the electrical conductivity values become constant, which is a strong indication that the thermodynamic equilibrium has been reached and there will be no more significant electrical conductivity variations, although the chemical reaction still occurs until the main reagents are consumed.

Fig. 4 - The Apparatus used during the tests

Therefore, in all cases, the kinetic studies evaluated the behavior of the reactions in the initial 20 minutes where the electrical conductivity was measured at each minute. Considering the fact that all the tests were conducted with diluted aqueous solutions of NaOH, the temperature and pH were measured for each test, but no significant variation was observed regarding these two variables.

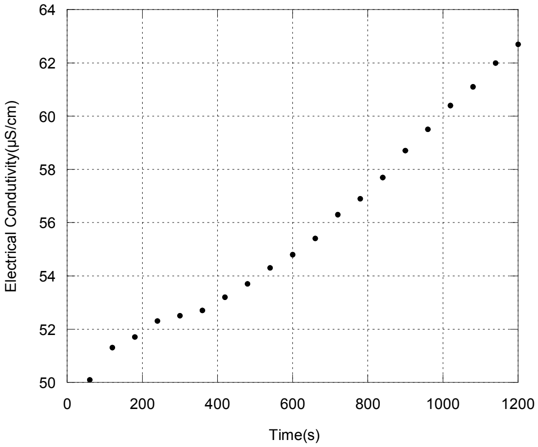


Fig. 5 - Experimental results of Electrical Conductivity (µS/cm±0.1) vs Time (s) for reaction between 0.25 mol/kg NaOH solution and flat pieces of solid aluminum (0.5 cm^2 and 0.2 mm thickness). The temperature T and the pH remained constant during the tests at (301.55±0.05) K and (13.00±0.05) respectively.

As mentioned in the item 3.1, the results of electrical conductivity can be converted in concentrations of NaOH after some mathematical manipulations. The next step is to prove mathematically and graphically the order of the reaction and this is the main reason why graphs involving logarithm neperian (NaOH concentrations) vs time must be obtained. It has been shown in each graph the linear trend with the adjustment of the regression model R^2.

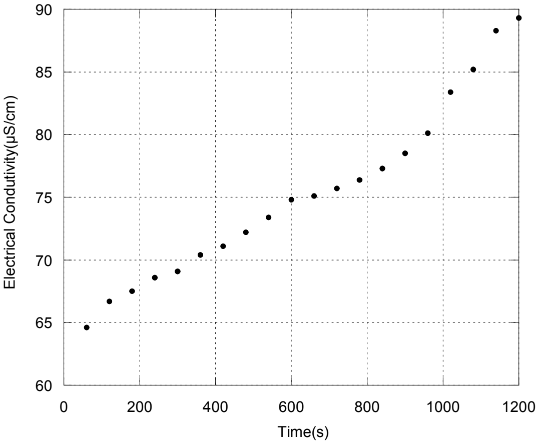


Fig. 6 - Experimental results of Electrical Conductivity (µS/cm±0.1) vs Time (s) for reaction between 0.50 mol/kg NaOH solution and flat pieces of solid aluminum (0.5 cm^2 and 0.2 mm thickness). The temperature T and the pH remained constant during the tests at (304.75±0.05) K and (13.20±0.05) respectively.

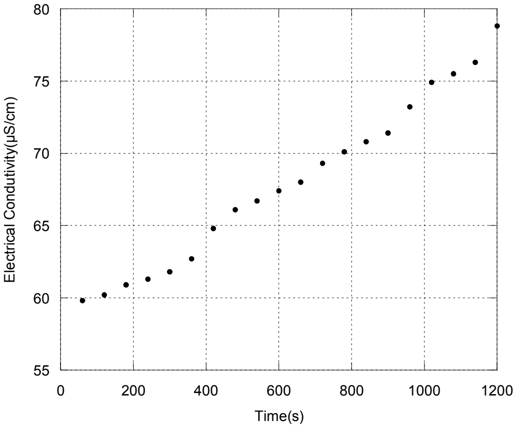


Fig. 7 - Experimental results of Electrical Conductivity (µS/cm±0.1) vs Time (s) for reaction between 0.75 mol/kg NaOH solution and flat pieces of solid aluminum (0.5 cm^2 and 0.2 mm thickness). The temperature T and the pH remained constant during the tests at (306.06±0.05) K and (13.72±0.05) respectively.

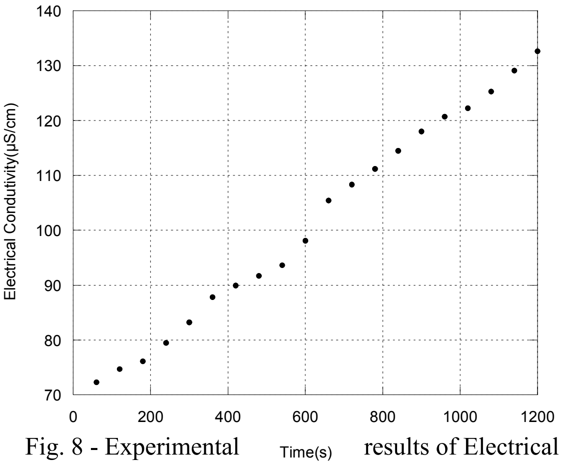


Fig. 8 - Experimental results of Electrical Conductivity (µS/cm±0.1) vs Time (s) for reaction between 1.0 mol/kg NaOH solution and flat pieces of solid aluminum (0.5 cm^2 and 0.2 mm thickness). The temperature T and the pH remained constant during the tests at (306.84±0.05) K and (13.85±0.05) respectively.

As expected, the reactions occurred faster as the concentration of the solution increases. Different concentrations of sodium aluminate were obtained while running the reactions and based on the mass balance it was possible to quantify the consumption of NaOH. These were the most important data obtained, since according to Fig. 9, 10, 11 and 12, it was possible to plot the consumption of NaOH versus time. For each concentration of the NaOH solution it was created a chart in order to identify if the reaction is really a first-order reaction in relation to the NaOH consumption.

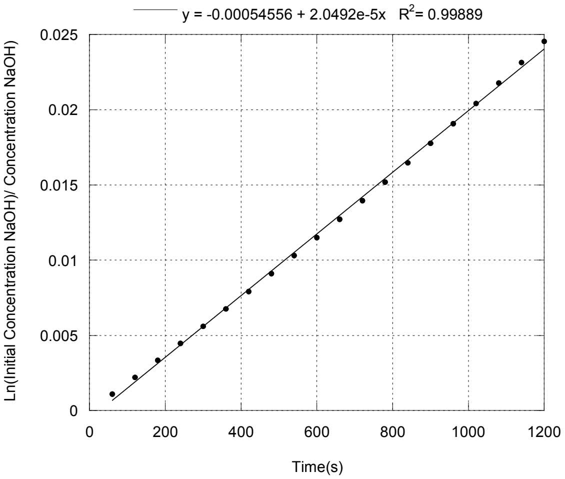


Fig. 9 - Relation between Ln (Initial concentration of NaOH/Concentration of NaOH) vs Time (s) for reaction with 0.25 mol/kg of NaOH solution.

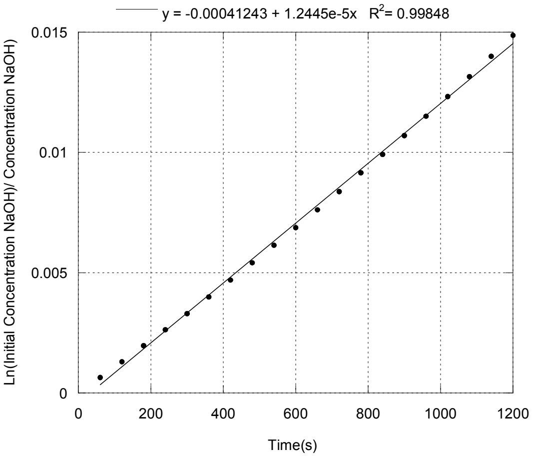
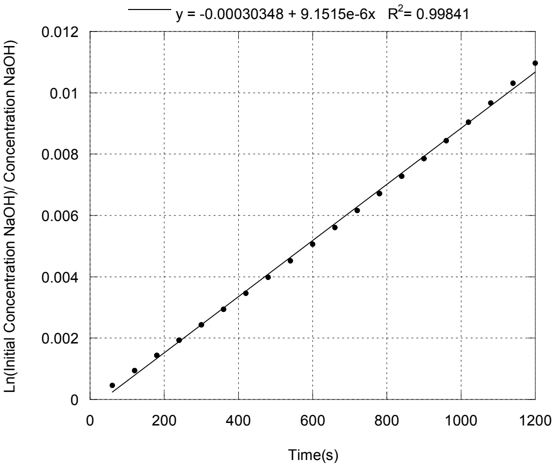


Fig. 10 - Relation between Ln (Initial concentration of NaOH/Concentration of NaOH) vs Time (s) for reaction with 0.50 mol/kg of NaOH solution.



11 - Relation between Ln (Initial concentration of NaOH/Concentration of NaOH) vs Time (s) for reaction with 0.75 mol/kg of NaOH solution.

For each chart there is a linear trend indicating that the chemical reaction between solid aluminum and an aqueous solution of sodium hydroxide is indeed a first-order reaction. The R-squared has showed a linear trend as high as 0.99 and this is a strong evidence that the order of the reaction was confirmed using conductometric method. Some references cited in this study have already confirmed the reaction order from the measurement of the volume of hydrogen generation, but in the present study the conductometric method proved to be effective and thus it can be said that the generation of hydrogen from the reaction between solid aluminum and aqueous sodium hydroxide solution is kinetically feasible, a first order reaction, spontaneous and exothermic.

The values of the pre-exponential factor, k_{app}= (10.71 ± 0.3) mol/s.m^2 and the activation energy of the reaction, E_a = (31.6 ± 0.5) kJ/mol were obtained, from the experiments with variation of temperature over time.

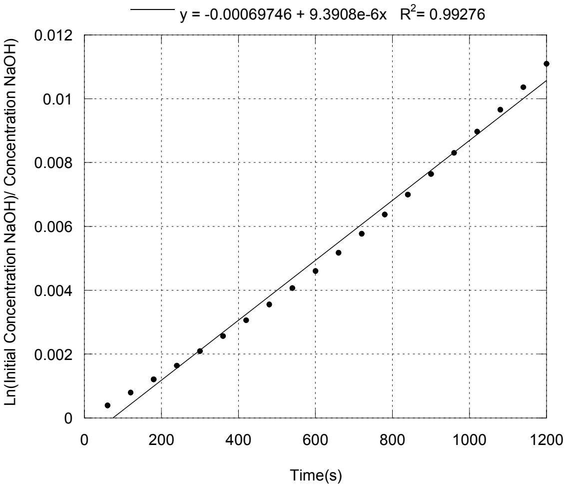


Fig. 12 - Relation between Ln (Initial concentration of NaOH/Concentration of NaOH) vs Time (s) for reaction with 1.0 mol/kg of NaOH solution.

Values slightly above were found in the literature [9,18] but the activation energy obtained in this work is in the same order of magnitude as the energy of hydrogen bonds, which confirm the ease (spontaneity) in which the chemical Eq. (1) takes place. We emphasize that the hydroxyl ions remove the oxide layer on the surface of the solid aluminum and allow the aluminum to react chemically. Thus, Eq. (22) represents the relation from which it is possible to obtain the constant of the reaction and using Eq. (12) it is possible to obtain the kinetic of the Eq. (1).

$$\ln \mathrm{k} = (10.71 \pm 0.3) + \\ - (31.6 \pm 0.5).\frac{10^3}{\mathrm{RT}}\left[\frac{\mathrm{mol}}{\mathrm{s}}.\mathrm{m}^2\right] \qquad (22)$$

Through mathematical manipulations and considering the consumption of sodium hydroxide, as well as the production of sodium aluminate, it is possible to carry out a mass balance and quantify the hydrogen generation. As a first qualitative analysis, a large production of hydrogen was observed; the reaction occurs very quickly and therefore must be controlled so that the final conversion (and consequently the yield) and the volume of gas produced can be attractive from the industrial point of view. In the tests conducted in this study it was verified that there is a strong formation of bubbles in the solution. The high bubbles formation was the main reason that the tests were conducted on a small scale, because otherwise, if high volumes were used, there would be an immense formation of gas, which acts as an insulator and therefore would make the electrical conductivities readings difficult.

It was evident that in diluted solution, as described in section 2, the steps occur spontaneously, without hindrance. In the tests with temperature varying with time, it was observed that the solution darkened, becoming grayish black. That confirms the strong presence of aluminate ion formation, as shown in Fig. 13. While the solutions were still at low concentration levels, there was no impediment in the formation of hydrogen or in the mass transfer of the gas from the sinus of the solution to the outside of the laboratory reactor.

The recycled aluminum proved to be highly reactive in the presence of a basic solution and the results showed that the kinetics of the reaction allows an idealization of an industrial reactors so that the production of hydrogen can be done in a renewable and sustainable way in industrial settings.

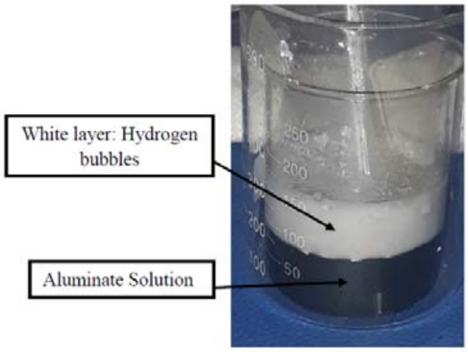


Fig. 13 – Feature of the solution with high concentration of aluminate ions.

The white layer above the black solution shown in the Fig. 13 is composed by bubbles of hydrogen formed when the reaction moves towards the thermodynamic equilibrium. Pieces of solid aluminum can be seen in the solution and were still reacting but when the solution became black the rate declined, the temperature decreased and specially, the volume of hydrogen, from a qualitative perspective dropped compared to the layer of bubbles during the beginning of the reaction, when the reaction rate was faster.

7. CONCLUSIONS

After concluding the experiments and the analysis of the results, some conclusions and suggestions are made as follows:

i. The kinetic is of first order regarding the consumption of sodium hydroxide;

ii. The reaction is spontaneous in ambient conditions and highly exothermic;

iii. A thermodynamic and thermal analysis must be carried out to verify whether the Eq. (1) can be thermally controlled in industrial reactors so that a renewable and sustainable chemical process can be developed for hydrogen generation and if in the same process, the recovery of the reactants can be economically sustainable from the Eq. (2);

iv. The volume to be obtained at the industrial level will be quantified only after a thermodynamic analysis of the Eq. (1), which will be the subject of the further studies.

v. It is known that the only industrially efficient processes that can recover solid pure aluminum from the Eq. (2) are the Bayer process and then the Hall-Heróult electrolytic process. Academia and industry need to join forces and research about new ways of obtaining solid aluminum not only from recycling waste aluminum but from aluminum hydroxide as well. This will ensure that a reliable process is feasible and attractive at industrial level.

vi. Since the reaction between solid aluminum and the aqueous solution of sodium hydroxide has a large release of energy as shown in the item 1.1, extreme caution has to be taken when designing reactors coupled to vehicles. With the present state of the art, an industrial reactor that produces a large amount of hydrogen should be designed so that the hydrogen can be stored and distributed to the network and supply enough fuel to vehicles.

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