Process and Device for Generating High Purity Hydrogen Based on Hydrolysis Reaction of Aluminum Dross

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Abstract-*This paper presents an efficient process to generate hydrogen, using aluminum dross particles activated by mechano-chemical methods and tap water with a pH value ≥ 10.4, obtained by adding of* NH_3 *aqueous solution 25 wt%/L. The effect of pH value and aluminum amount on hydrogen yield has been studied. For these tests pure aluminium particles and aluminum dross were employed, and SEM analysis was used to study the changes in surface properties of metal occurring due to metal hydrolysis and hydrogen release. The obtained results show that the rate of hydrogen generation increases with the increasing of pH value and aluminum quantity. A hydrogen continuous device was designed and operated. The economical and environmental key aspects associated with the production of hydrogen, using Al dross, are discussed. The data obtained in this research can provide the basis for scale implementation of the aluminum dross hydrolysis process to generate* H_2 *of high purity (>99.5 vol.%).*

Keywords: aluminum dross; aluminum-water reaction; hydrogen generating; tap water; mechano-chemical activation;

I. INTRODUCTION

Progress of energy systems depends on the development of new efficient and environmentally sustainable sources of clean energy. There are several ways to develop such sources. One way of perspective is based on the generation of hydrogen [1-3]. Hydrogen is known as one of the best clean energy carrier because of its minimal impact on the environment regarding to greenhouse gas emissions such as carbon dioxide and other gases [1, 4-6]. Hydrogen can be used directly in molecular form , (i.e. as a fuel for vehicles) or indirectly to generate electricity for other industrial applications [4-7] .A major advantage which it has over other fuels is that not cause pollution because of its burning reaction results only water. Hydrogen is also an almost ideal fuel gas and in terms of reducing smog when it is burned. However, safe storage and generation at low cost are technical challenges that need to be considered. For these reasons there are sought new ways to produce hydrogen at low cost from other sources than are known [8-10].The alkali metals (such as sodium, potassium, lithium) and alkaline earth (calcium, strontium, aluminum, magnesium, etc.) are very active when they come in contact with water, react spontaneously, generating hydrogen and heat. Based on this chemical property, the hydrolysis reaction of pure aluminum powder is commonly used for high purity hydrogen generation [6, 11,12,13, 14].Although the use of pure aluminum in reaction with water to produce hydrogen is a viable method, it is expensive, if it takes into account the cost of producing pure aluminum and the use of an alkali metal hydroxide, also an expensive product. The alkali metal hydroxide is used to remove the protective layer of aluminum oxide on the surface of the aluminum particles, which prevent the contact between the metal and water, and thus slow down or substantially avoid reaction between the aluminum and water [15, 16, 17, 18] .As a result, other methods should be studied and utilized to activate the surface of the aluminum particles, to initiate and accelerate the reaction of hydrolysis. Different methods to enhance the rate of aluminum reaction and other metals with water have been developed [19,20, 21, 22].One such method is mechanical activation (crushing, cutting, grinding). This is a method not so expensive and leads to removal of aluminum oxide layer and obtaining a surface clean and active. Also, the replacement of an alkali metal hydroxide with less expensive other chemical compound [19] can be effective. Another way to reduce the costs is to replace pure aluminum with another source of aluminum. As is known from the literature, large amounts of aluminum are present in the solid metal wastes resulting from the production of aluminum, or from recycling processes, this being known as dross or slag [10, 12.13]. The use of this source of aluminum to generate hydrogen has both benefits to environment by waste recycling, and to the cost of hydrogen producing, that decreases substantially. In this work, we have investigated the hydrolysis properties of Al powder and Al dross mechanically treated by ball milling to form a fresh chemically active metal surface, with the use of tap water, in which was added a small amount of ammonia solution 25 wt %, to increase the pH (i.e. from 6.95 to 10.45) and to create a strong alkali environment that determines the metal surface activation. The aim is to accelerate the hydrolysis rate and to improve the hydrogen yields of the mixture in water. Removal of the aluminum oxide layer on aluminum particle surface by mechanical means, sustains aluminum assisted water split reaction. In addition, the presence in dross composition of an effective amount of nitride (AlN), salts, especially KCl, NaCl, and oxides such as CaO and MgO, with metal, more so in Al dross, play the role of catalysts for the reaction between Al and water. Once contacted with water, these compounds cause substantial increase of pH (i.e. create a higher alkaline environment, increasing the pH value from 10.45 over 12.4) which accelerates the corrosion of Al with accompanying of hydrogen release. The activated aluminum can then react spontaneously with water, even at room temperature, without adding any chemicals to the water and hydrogen is produced.

II. MATERIALS AND METHODS

The aluminum dross used in our experiments was supplied by S.C. AL Mina Com SRL, Bucharest, Romania. The samples consisted of rounded lumps up to approximately 10-15 mm in size (as well as some smaller metallic fragments) and had a slight smell of ammonia. The samples were grinded and for this it was used a Fritsch planetary mill, with stainless steels balls and vials and then the ground material were sieved through a 100-µm aperture screen. A sample before and after grinding is shown in Fig. 1(a, b).


(a) (b)

FIGURE 1. Sample of aluminum dross before (a) and after grinding (b)

The chemical analysis of the elements of raw aluminum dross was carried out by atomic absorption spectrometry method using an analyzer type Analytic Yena Nova 300, X-ray diffraction, using a Philips PW 1710 diffractometer with Ni filter and Cu kα radiation and the morphology of the powders was analyzed using scanning electron microscope JSM-7500F (JOEL-Japan) operated at 10Kv, and X-ray fluorescence (XRF) method, using an analyzer type Bruker S1 Titan 600. A composition is presented in Table 1.

TABLE 1
The composition of raw aluminum dross

Composition	Al	Al_2O_3	AlN	MgO	Fe_2O_3	KCl	NaCl	SiO_2	CaO
Mass wt%	15.27	43.71	7.2	4.28	4.35	5.94	7.38	10.09	1.78

Other starting materials used in experiments were: powder of pure Al, size approximately 45-100 µm (99.5% purity) supplied by Alfa Aesar, a Johnson Mathey Company; nitrogen and argon gases (N_2, Ar) with a purity of 99.99% purchased from Linde Company, ammonia solution 25 wt% supplied by Adra Chim SRL Bucharest, Romania, ferrous sulfate supplied by Sigma-Aldrich, zeolite molecular sieve 5Å from Linde Company.

Surface of aluminum particles were activated by mechanical grinding and also using tap water with an alkaline pH ≥10.4. First, by adding 2 ml aqueous ammonia solution 25wt% / L_{H2O}, the pH value of water increased from initial value of 6.95 to a value of 10.45. This tap water with high pH, in contact with Al dross particles, which contain appreciable amounts of AlN, salts and other alkaline oxides , accelerates the hydrolysis reaction of AlN and these compounds leading to releasing of high soluble alkaline compounds which also determines the increase the pH value over 12.4.Consequently, this high alkaline environment accelerates the corrosion process of Al particles and releases hydrogen.

For experiments it was used a laboratory system consisting of a flat-bottomed glass flask with a volume of 500 ml., a hot plate with magnetic stirrer and water bath, (Fig. 2). The reaction started by introducing of 200 ml alkaline tap water (obtained by adding 2 ml ammonia aqueous solution of 25wt% /$L_{tap\ water}$) or tap water without adding ammonia solution, through the central vessel neck over 1 to 3 g of pure Al particles or over 6.548 to 19.646 g of Al dross particles respectively, also containing an amount of Al of 1 to 3 g and which were poured in the flask from beforehand. After Al particles or aluminum dross particles were introduced, the neck of flask was immediately corked and before tap water or tap water solution introducing, the entire system was purged with nitrogen gas at a flow of 60 ml/sec for 10 min. This operation was performed to remove air from the system and to prevent formation of an explosive mixture with the hydrogen released from reaction. The temperature of the process was measured and for this it used a Chromel/Alumel thermocouple.

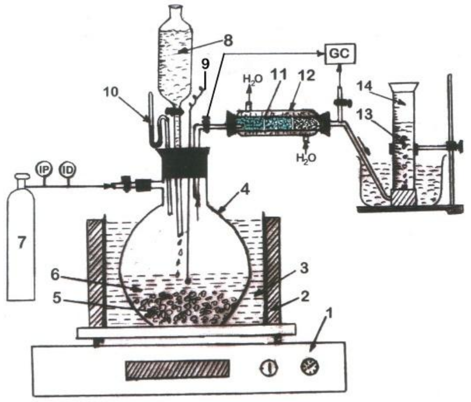


FIGURE 2. Laboratory experimental system:(1) magnetic stirrer ; (2) electric stove ; (3) water bath; (4) flat-bottomed glass flask ; (5) pure Al powder or Al dross powder; (6) tap water or alkaline tap water solution; (7) tank containing nitrogen under pressure; (8) burette containing tap water or alkaline tap water solution; (9) thermocouple; (10) manometer; (11) filter containing zeolite molecular sieve 5Å and iron sulphate ;(12) cooler; (13) gas burette graduated at room temperature in 0.1 ml increments, filled with deionized water for hydrogen gas volume collecting; (14) hydrogen volume collected; (GC) gas chromatograph; (IP) pressure indicator; (ID) flowmeter.

The flat-bottomed glass was placed in bath filled with water maintained at room temperature to prevent overheating. The gas was passed through a filter to remove water content and to retain ammonia, and then the volume of hydrogen was measured. For this, the outer walls of the filter were cooled using colder water (5-10 ^{O}C), and the filter was filled with layers consisting from zeolite molecular sieve 5Å and iron sulphate ($FeSO_4.7H_2O$). The volume of hydrogen released was determined by the water trap method and corrected at standard temperature and pressure (STP). Atmospheric pressure was established of local weather office. All experiments were performed at a temperature of 20^{O}C and an atmospheric pressure of 759 mm of Hg. The hydrogen gas released was directed into an inverted burette of 1000 to 2000 ml, containing deionized water. The hydrogen gas has displaced the water from burette, and the changing of the water level in the burette was noted as a function of time. The rate of change of the water level in the burette is determined by the production rate of hydrogen in the hydrolysis reaction and the difference between the initial and final water level represents the total volume of hydrogen generated. At regular intervals (1.2, 3 or 5 minutes) were collected gas samples, using gas-tight syringe of 1 ml. Then it was determined gas composition and the purity of H_2 released from reaction. The gas composition was established bygas chromatography method, using agas chromatograph type HewlettPackard5890A. This was equipped with two detectors, (flame ionization and thermal conductivity) two columns (Porapak-Q and5Amolecular sieve) and it was used as carrier as argonor helium, depending on the components which were determined. To study the hydrolysis reaction between aluminum and water were made two types of experiments. In the first set of experimental tests has been used the laboratory system shown in Figure 2, pure aluminum powder and aluminum powder dross. The data obtained were compared between them regarding the volume of hydrogen released from the reaction of aluminum with tap water, with or without addition of ammonia. The influence of parameters such as pH value and aluminum amount on aluminum-water reaction rate and hydrogen yield was studied. As a result of this original process, it was designed and assembled a hydrogen generation device and then it was evaluated the process of continuous release of hydrogen from the reaction of the mechanically milled aluminum dross with alkaline tap water(containing 2 ml ammonia aqueous solution of 25wt% /$L_{tap\ water}$).

III. RESULTS AND DISCUSSION

3.1 Reaction of aluminum with water

The concept of hydrogen production by the hydrolysis reaction of alkaline or alkaline-earth metals with water is known [2, 3]. More recently, these researches were enhanced and this is reflected in an increased number of publications and patents that are directed to the hydrogen production, through reactions between water and aluminum based metal [5-7]. All of the aluminum based approaches propose activation methods to remove the protective layer of aluminum oxide, thus allowing the hydrolysis reaction to start and proceed. The following exothermic reactions are possible when activated aluminum particles come in contact with water:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad + \Delta H \tag{1}$$

$$2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2 \quad + \Delta H \tag{2}$$

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

The first reaction forms the aluminum hydroxide ($Al(OH)_3$) known as bayerite and hydrogen, from the second reaction results the aluminum hydroxide ($AlO(OH)$) known as boehmite and hydrogen , and from the third reaction results aluminum oxide (Al_2O_3) known as alumina and hydrogen. All above reactions are thermodynamically possible from room temperature till the aluminum melting point ($660^{O}C$) and are highly exothermic. The thermodynamic of all above reactions indicate that aluminum could spontaneously react with water, but in practice if a piece of aluminum is dropped into water under room temperature or even with boiling water conditions will not react, because the aluminum surface has an adhering and thin coherent layer of oxide (Al_2O_3), which prevents the reaction. Therefore, the key to starting and maintaining the reaction of water with aluminum at room temperature is the permanent disruption and removal of the hydrated alumina thin layer on the surface. In this work the activation method of aluminum dross particle surface is based on mechano-chemical technique, including the mechanical milling method and analkaline environment with high pH value. Bymechanical milling of aluminum dross are obtained particles to size ≤ 100 µm and was removed the protective layeron the surface of aluminum particles, thus favoring the onset of reaction. Also, the presence of nitride (AlN), salts in sufficient quantity, in particular KCl, NaCl, and oxides such as CaO, MgO (Table 1), when mixed with metals other than aluminum, acts as a catalyst for the reaction between Al and water. Also, a strong alkaline medium dissolves the oxide layer on the surface of the aluminum particles. In most studies this alkaline environment is created by adding an alkali hydroxide (NaOH or KOH)[4, 11]. Analyzing the dross composition (Table 1) it can be seen that contains AlN and Na and K salts (NaCl, KCl). As shown in other studies [22,23]on hydrolysis behavior of AlN in water and different solutions it was found that this hydrolyzes faster and more efficient in alkaline solutions. Hydrolysis process occurs according to the reactions:

$$AlN + 2H_2O \rightarrow AlOOH + NH_3 \tag{4}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{5}$$

$$AlOOH + H_2O \rightarrow Al(OH)_3 \tag{6}$$

According to the reaction (4) by hydrolysis of AlN result NH_3 that rapidly dissolves, according to the reaction (5) and leads to an increase in pH value of the water and helps to solubilize and remove the protective oxide layer. In our experiments, the high alkaline environment was created , first, by adding of 2 ml NH_3aqueous solution of 25wt% /$L_{tap\ water}$ to stimulate the hydrolyze of AlN, and then by salts of sodium, potassium and calcium oxides , which are present in the initial composition of the dross (Table 1) and in contact with water also hydrolyze and cause an increase in pH value. In Fig. 3 is presented the changing in pH value, using different amounts of ammonia aqueous solution of 25wt% / $L_{tap\ water.}$

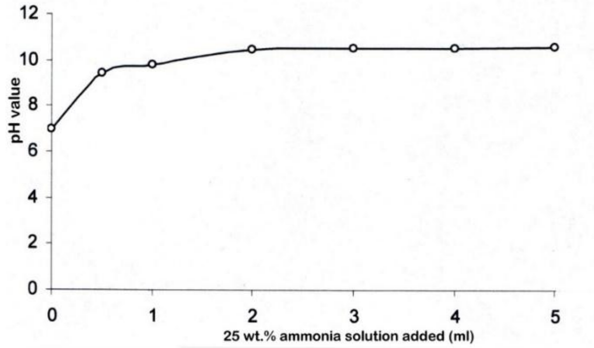


FIGURE 3. The pH value variation by adding of different quantity of NH_3 aqueous solution of 25wt% /$L_{tap\ water}$

By adding 0.5 ml, 1 ml and 2 ml aqueous ammonia solution 25wt% / $L_{tap\ water}$, the pH value of tap water increased from initial value of 6.95 to a value of 9.43, 9.81 and 10.45 respectively. Further increase in the amount of 25 wt% aqueous ammonia solution / L has not led to a substantial increase in pH value, this remaining almost constant (Fig. 3).As a result, the amount of 2 ml aqueous ammonia solution 25wt% / $L_{tap\ water}$ has been used to create a water with an pH of 10.45, enough to accelerate the AlN, NaCl, KCl, CaO and MgO hydrolysis reactions and to lead to an increase of pH value (≥12.4). This higher alkaline environment accelerates the Al corrosion process, removing the oxide layer on the Al particle surface by its solubilizing and releasing the hydrogen.

Using the laboratory system presented in Fig. 2, some experiments were performed in order to get more details on hydrolysis reaction regarding certain factors affecting the reaction rate and hydrogen yield, such as pH value and aluminum amount. In a first experiment , 71.1ml of gas was obtained in 15 min, using 1 g of Al powder (≤ 100 µm) with 200 ml tap water having the value pH of 6.95, at the room temperature (Fig 4a, Table 2).

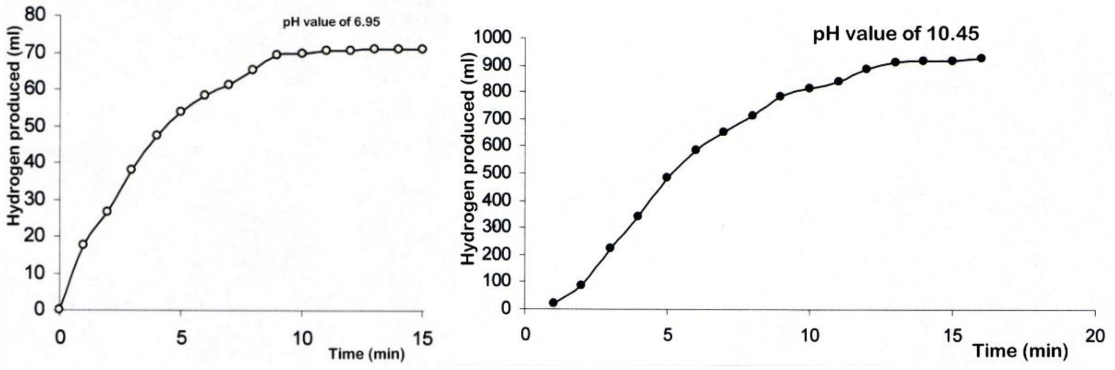
TABLE 2
Hydrogen volume released from reaction of 1g Al powder (≤ 100µm) with 200ml tap water (without NH_3 solution 25wt.%), pH= 6.95

Time (min)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$H_{2released}$(ml)	7.6	26.4	38.1	47.3	53.8	59.5	61.4	65.2	69.2	69.9	70.6	71.1	71.3	71.2	71.2	71.23

TABLE 3
Hydrogen volume released from reaction of 1g Al powder (≤ 100µm) with 200ml tap water (with 2 ml NH_3 solution 25wt.%/$L_{tap\ water}$), pH= 10.45

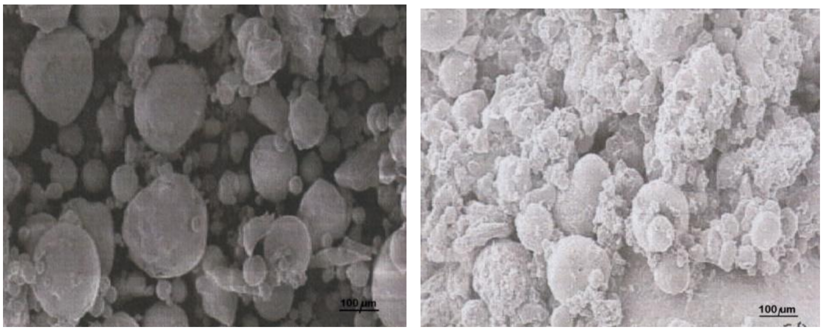
Time (min)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$H_{2released}$(ml)	20.4	48.7	66.8	74.9	83.5	167.1	250.5	334.2	417.5	503.2	584.5	667.8	751.2	853.2	919.6

In this case, the hydrolysis reaction rate was found to be slowly. Figure 4b and Table 3 present the rate of hydrogen production using 1 g Al powder, 200 ml tap water having the pH value of 10.45, at the room temperature. Analyzing this experiment, it may be observed that the rate of H_2 production during the first minutes is high, that means the rate of Al corrosion particles is also high. From first minute to 12th minute, the production rate goes on increasing and after the production remains almost constant with time. The morphology of initial Al powder is presented in the SEM images, Fig. 5. It can be observed that it consists of a lot of spherical particles of different size diameters, from 20 µm to 100 µm. Reacted Al particles coexist with the unreacted particles, and there are even the particles partially covered with products of hydrolysis reactions.



(a) (b)

FIGURE 4. Hydrogen production using 1 g Al powder with particle size ≤100 µm, 200 ml tap water having the pH value of 6.95 without ammonia solution adding (a) and the pH value of 10.45, by adding 2 ml ammonia solution of 25%/$L_{tap\ water}$ (b), at room temperature.



(a) **(b)**

FIGURE 5. SEM images of microstructures of Al particle surfaces: initial Al particles (a) and after hydrolysis with tap water at pH 10.45 for 15 mins (b) at room temperature

Catalytic reaction of aluminum with water produces an important heat quantity and hydrogen gas. As was stated, the presence in dross composition of an effective amount of nitride (AlN), salts (NaCl, KCl), oxides such as CaO, MgO, they play a role of catalyst. Starting at 20^{O}C, the temperature in the reactor was modified according to the graph from Fig. 6. There is a period of a few minutes for the heating phase, after which the temperature is stabilized at about 45.2 ^{O}C. After about 18 minutes, the temperature drops, reaching within minutes at about 21 ^{O}C, indicating the exhaustion amount of aluminum in reaction with the water.

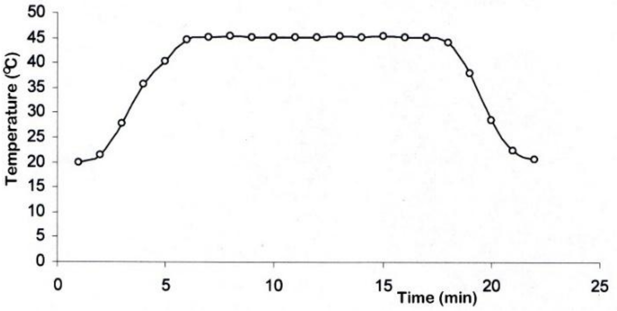


FIGURE 6. Variation of temperature over time for the reaction of hydrogen gas production (temperature of 20^{O}C; 1 g Al powder with particle size ≤100 µm, 200 ml tap water with a pH of 10.45)

Fig. 7 and Table 4 show the hydrogen volume produced using different aluminum amounts (1, 2 or 3 g Al powder respectively) and 200 ml tap water having a pH value of 10.45 for each experiments, obtained by adding 2 ml ammonia solution of 25%/L$_{\text{tap water.}}$

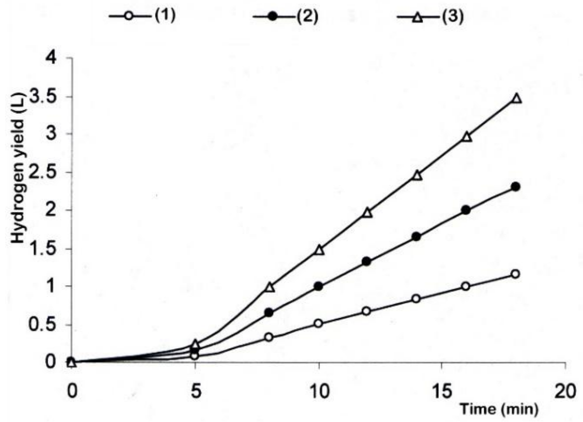


FIGURE 7.Hydrogen production using 1 g, 2g and 3g Al powder respectively ,with particle size ≤100 µm, 200 ml tap water having a pH value of 10.45 obtained by adding 2 ml NH_3 solution of 25%/L , at room temperature.

TABLE 4
Hydrogen volume released from reaction of 1g, 2g and 3g Al powder (≤ 100µm) and 200 ml tap water (with 2 ml NH_3 solution 25wt.%/L$_{\text{tap water}}$), pH= 10.45

Time (min)								H_2 (L) $_{\text{calc}}$	Yield,η (%)
	5	8	10	12	14	16	18	(18 min)	
(1g Al)	0.083	0.334	0.503	0.667	0.835	1.002	1.169	1.244	93.97
$H_{2released}$ (L) (2gAl)	0.163	0.661	0.991	1.322	1.648	1.990	2.311	2.488	92.88
(3g Al)	0.247	0.997	1.491	1.971	2.478	2.976	3.486	3.732	93.41

Average efficiency = 93.42 %

Analyzing the data obtained from these experiments, it may be concluded that the H_2 production is high. From first minute to five minutes, the H_2 volume produced increases slightly, after the H_2 volume produced increases rapidly; the production rate is nearly constant (Table 4).The H_2 volume produced is close to that theoretical. The effect of increasing of Al amount on the hydrogen volume produced also can be seen in Fig. 7 and Table 4. The amount of hydrogen produced increases almost linearly with the amount of aluminum used. For example, when using 2 or 3 g Al, at the same reaction time, the hydrogen volume released is almost double or triple, compared to that obtained from 1 g Al, the reaction efficiency being higher than 93%.

3.2 Reaction of aluminum dross with water

Using the same laboratory system (Fig. 2) the pure Al powder was replaced by an appropriate amount of Al dross (Table 1) that to contain the same amount of Al such as: 6.548g Al dross containing1 g Al;13.097g dross, containing 2 g Al and 19.646 g dross containing 3 g Al, respectively. Fig. 8 and Table 5 show the hydrogen volume produced using these aluminum dross amounts and 200 ml tap water containing 2 ml NH_3aqueous solution of 25wt% /L $_{\text{tap water}}$, having a pH value of 10.45.

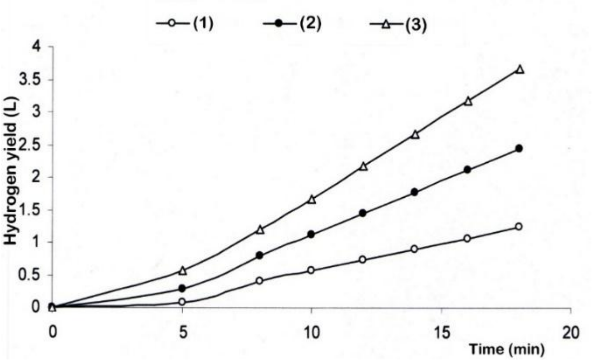


FIGURE 8. Hydrogen production using 6.548, 13.097 and 19.646 g Al dross respectively, size particles ≤100µm, tap water with pH value of 10.45, room temperature.

TABLE 5

Hydrogen volume released from reaction of 6.548g, 13.097g and 19.646g Al dross powder (≤ 100µm) and 200 ml tap water (with 2 ml NH_3 solution 25wt.%/$L_{\text{tap water}}$), pH= 10.45

Time (min)	5	8	10	12	14	16	18	H_2 (L) $_{\text{calc}}$	Yield,η (%) (18 min)
(6.548g Al dross)	0.089	0.402	0.566	0.734	0.897	1.067	1.235	1.244	99.29
$H_{2\text{released}}$ (L)(13.097gAl dross)	0.277	0.798	1.123	1.453	1.784	2.114	2.447	2.488	98. 37
(19.646g Al dross)	0.565	1.197	1.683	2.184	2.673	3.176	3.672	3.732	98.39

Average efficiency = 98.68%

Adding 200 ml of tap water having a pH value of 10.45 over 6.548g; 13.097g and 19.646 g Al dross respectively, the pH value was increased (≥ 12.4), this increase being due to hydrolysis of AlN, salts, calcium and magnesium oxides present in the dross composition. Increasing of the pH value leads to speeding up the activation surface of aluminum particles, potentially reactive with water, according to reactions (1, 2, 3). In Figure 8 is shown the H_2 volume released during the reaction of Al dross powder ,size particles ≤100µm, with 200 ml tap water containing 2 ml ammonia aqueous solution of 25wt% /L and having a pH value of 10.45, at room temperature. Al dross powder showed almost no apparent reaction with tap water of 6.95 pH, whereas in tap water of 10.45 pH, aluminum exhibits effervescent reaction with hydrogen release. Analyzing the data obtained from these experiments, it may be concluded that the H_2 production is high. From first minute to five minutes, the H_2 volume produced increases slightly, after the H_2 volume produced increases rapidly; the production rate is also nearly constant (Table 5).The H_2 volume produced is very close to that theoretical. The effect of increasing of Al dross amount on the hydrogen volume produced also can be seen in Figure 8. The volume of hydrogen produced increases almost linearly with the amount of aluminum dross used. For example, when using 13.097, 19.646 g Al dross, at the same reaction time, the hydrogen volume released is almost double or triple, compared to that obtained from 6.548 g Al dross,the reaction efficiency is > 98% and this being higher than that in case of using pure Al powder (>93%), see Table 4 .This could be explained by creating a higher alkaline environment that resulted from solubilization of AlN, sodium and potassium salts, as well as of CaO, MgO in reaction with the water (e.g achieving a pH of 12.45 instead of 10.45 pH value) and which accelerates the activation process of Al surface and Al reaction with water, releasing hydrogen, or even the hydrolysis reaction of the other metals present in the composition of the dross, releasing of hydrogen as well. The composition of the gas product was determined at the exit of the reactor and an average is: 98.42 vol.% H_2; 1.26 vol.% NH_3; 0.11 vol.% N_2; 0.21 vol% H_2O.The hydrogen purity after passed through the filter, where was retained the moisture and NH_3 was also determined . An average value obtained was 99.73vol.% H_2. The HN_3 was removed by chemosorption process using ferrous sulfate, according to the reaction (7)

$$3[FeSO_4.7H_2O] + 3NH_3 \rightarrow 3(NH_4)_2SO_4 + Fe_3O_4 + 17H_2O + H_2\uparrow \tag{7}$$

The reaction is fully, the entire quantity of NH_3 from hydrogen produced is retained. The calculation of the necessary quantity of $FeSO_4.7H_2O$ was done in accordance with the reaction stoichiometry. Humidity has been reduced from 0.21vol. % to 0.05 vol. %, by adsorption on zeolite molecular sieve 5A. Hydrogen generation rate is very important in this process and it can be determined by variables that can be controlled as hydrogen yield calculated with equation (8):

$$\eta\%H_2= (nH_2(t)/nH_2O)x100 \tag{8}$$

where nH_2O is the number of water moles consumed in the reaction and reaction rate is given by equation (9):

$$v(H_2)=dv(t)/dt \tag{9}$$

3.3 Hydrogen generating device based on aluminum dross hydrolysis process

Based on experimental data obtained, a continuous hydrogen generating device was designed and assembled and hydrogen volume produced during the hydrolysis reaction of mechanically milled aluminum dross with tap water containing 2 ml ammonia aqueous solution of 25 wt% /L was evaluated. The scheme of the steps taken for hydrogen production is presented in Fig. 9 and the schematic device is shown in Fig. 10. The characteristics of reactor were described in reference [24]. The cartridge was designed as a perforated basket, lined with felt on the inside wall and it was filled with aluminum powder dross (≤100μm). Lining cloth was used to prevent the passage of dross particles through the holes of basket wall and to ensure continuous absorption of water from the tank and also to allow the leakage of the gas released from the reaction of aluminum particles with water through holes.

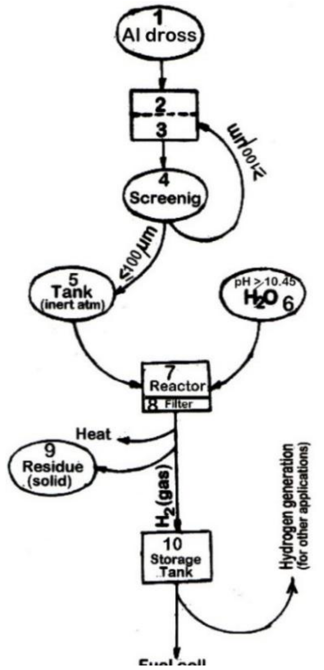


FIGURE 9. Schematic representation of the steps taken for hydrogen production process using aluminum dross and water

Hydrogen generating process as schematically is presented in Fig. 9, is based on the reaction of aluminum dross with water and includes several stages. The use as raw material of the aluminum dross is expected to result in the form of pieces of different sizes (Fig. 1 a) from the primary and secondary production of aluminum metal from or (bauxite) or recovered scrap from various sectors such as automotive, cans, beer, construction, etc. Hard dross (1) is crushed by crushing (2) and then converted into powder by milling (3), for this operation using a ball mill. Milling stage is followed by screening stage(4) for fraction separation containing particles with size $\Phi \leq 100$ μm , which are stored in the tank (5) under an inert atmosphere of argonto maintain the active surface of the aluminum metal particles. Fraction consisting of particles $\Phi \geq 100$μmsizeis returnedin(3) for regrinding and resorting. Powder in the tank (5) with $\Phi \leq 100$ μm particle sizes is used to fill the reactor cartridge (6). From the tank (7) it is inserted into the reactor (6) water (tap or industrial water, containing 2 ml NH_3 solution of 25 wt. %/L). At contact between water and aluminum particles, which were activated on the surface by mechanical grinding, inreactor (6) takes place first the phenomenon of hydrolysis of AlN, salts of Na, K and oxides of Ca and Mg, present in the composition of the dross, resulting in an increase of alkaline pH from 10.45 to ≥12.4) in the reaction area, an environment that favors the onset of the reaction between metal particles of active Aland water to obtain hydrogen of high concentration(> 99.5% vol) and release heat , according to reactions(1 - 3).

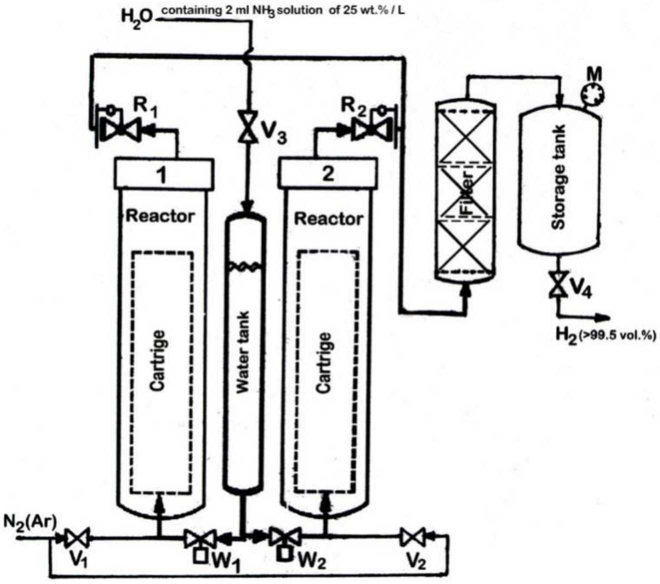


FIGURE 10: A schematic representation of hydrogen production system: (1) and (2) reactors containing fuel cartridge filled with Al dross powder; water tank; filter containing zeolite molecular sieve 5Å and $FeSO_4.7H_2O$; M – manometer; R_1, R_2 –three-way valves; V_1,V_2,V_3, V_4 – valves; W_1,W_2-water valves;

A schematic representation of hydrogen generating device is presented in Fig. 10. The capacity of the device is of about 2 kg of Al dross powder (≤ 100 μm) for each reactor, which contains about 305.4 g Al. The initial temperature is room temperature. The gas released from the reaction passes through the layers consisting of molecular sieve 5A and ferrous sulphate from the filter. Here, the hydrogen gas is purified by removing moisture and ammonia. Further, the hydrogen is collected in the storage tank. First reactor unit worked continuously ≈ 9 h at a hydrogen generation rate of about 0.735 L/min. The purity of hydrogen produced was 99.58vol %. After about 9 hours of operation, the reactor (1) was disconnected by closing water valves (W_1) and R_1, while was connected the reactor (2) by opening water valves (W_2) and R_2, thus ensuring continuous operation of the device. Hydrogen gas resulted can be taken by the user (eg. a fuel cell or industrial applications, Fig. 9).The data obtained in our research can provide the basis for scale implementation of the aluminum dross hydrolysis process to generate hydrogen. We have reached the very important conclusion that by hydrolysis process of aluminum waste such as Al dross can be obtained hydrogen of high purity (>99.5 vol.%).

IV. KEY ASPECTS ASSOCIATED WITH THE PRODUCTION OF HYDROGEN USING Al DROSS

As mentioned, thhydrolysis reaction of the pure aluminum metalis typically used for the production of hydrogen. Although the use of pure aluminum in reaction with water to produce hydrogen is a viable method, it is expensive, if it is considered the cost of producing aluminum in the form of pure metal and alkali hydroxide consumption, also an expensive product. The key aspects associated with the production of hydrogen using the aluminum metal-water reaction are as follows: Aluminum required: 9kg Al per 1kg H_2 produced, considering 100% yield; A gravimetric hydrogen capacity of 3.7 wt.% (materials only); A volumetric hydrogen capacity of 36-46 khH_2/L (materials only); Reaction kinetics: $2x10^{-4}$gH_2/sec/g of Al [25];A production cost: ≈ € 5.7 per kg H_2 (based on the cost of electricity for aluminum production and considering only the reduction of alumina to metal aluminum step) [25,26].If there are considered and the steps required to produce alumina from bauxite and alkali hydroxide consumption required in hydrolysis reaction, certainly the costs are much higher. From published data to date [25, 26],the worldwide the aluminum industry produces over 4.5 billion kilograms of aluminum waste per year. Each type of waste has unique physical and chemical characteristics, and the waste value is determined by the level of impurities contained and the cost required for metal recovering. Taking into account the chemical composition of aluminum dross presented in Table 1, it follows that1 kgof dross contains 0.1527kgAl, amount that can react with water to produce hydrogen and aluminum oxy-hydroxide or other Al compounds. Alkali hydroxide consumption is zero, in this case , the alkaline reaction medium is ensured by adding of 2 ml ammonia aqueous solution of 25wt% /L water used, (meaning a very small quantity), and this being much cheaper than an alkali hydroxide and also by the content of AlN , Na, K salts and Ca, Mg oxides, present in the dross composition(as we noted in the description presented above).By extrapolation, 9 kgAl needed to produce1 kgH_2 (considering 100% yield) corresponding to an amount of≈ 59 kg dross. Since this is a waste (with negative consequences on the environment by landfill), its use to produce hydrogen and other high value products (aluminum oxy-hydroxide, alumina, etc.) leads to a viable and advantageous solution because capitalizes a possible hazardous waste to the environment and people and reduces significantly the cost of hydrogen production. Also, it solves an environmental issue by reducing the negative environmental impact and it leads to lower energy and raw materials consumptions necessary for obtaining pure aluminum metal and alkali hydroxide, materials involved in the reaction with water to release hydrogen. Other resulting benefits cover issues such as reducing the volume of aluminum waste disposed in landfills, conserving energy and natural resources used to produce new aluminum amounts, reducing landfill disposal fees, generating of new renewable energy sources and encouraging the recycling of other kinds of wastes. Recycling aluminum waste can only bring benefits to society at lowering the cost of production for a big number of products that are used every day, among them being and the hydrogen. Maybe people should be encouraged to reuse this material if they know some basic statistics such as that a piece of aluminum naturally disappear after 100 years, but by recycling it could save energy to produce 20 pieces of recycled. The ore from which obtain aluminum is bauxite and current reserves of bauxite are sufficient for another 400 years, but recycling 1kg of aluminum it could save ≈ 8 kg of bauxite, 4 kg of chemicals and 14 kWh of electricity[26],obvious benefits both economical and energetical. Also, the fact that hydrogen will become certainly clean energy source for the future, should be supported the processes of its obtaining , starting from such sources of cheap raw materials, which will lead to reduction in the cost of production.

V. CONCLUSIONS

An investigation of hydrogen production using aluminum dross and tap water with high pH value (≥10.45) was made. The experiments conducted at laboratory scale allowed determining the amount of hydrogen generated and processing temperature. Data obtained showed that the fast and self sustained hydrolysis reaction of activated Al dross particles with tap water, whose pH was increased from 6.95 to 10.45 by adding of 2 ml ammonia aqueous solution of 25wt% /L, takes place, starting from the room temperature and can release hydrogen of high purity(>99.5 vol.%). Based on experimental laboratory data, a continuous hydrogen generating device was designed and operated. Its operation shows clearly that Al dross can be successfully used for producing hydrogen of high purity. The key aspects associated with the production of hydrogen, using Al dross, certainly present only benefits to society, contributing to lowering the cost of hydrogen production and to solve an environmental issue by reducing the negative impact. The data obtained in our research can provide the basis for scale implementation of the aluminum dross hydrolysis process to generate hydrogen. This process is based on aluminum hydrolysis, consuming only water and aluminum dross which are cheap raw materials. As a consequence, this process could be a feasible alternative for CO_2 free hydrogen production for fuel cell or other applications.

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