



Hydrolysis of aluminum dross material to achieve zero hazardous waste

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ABSTRACT

A simple method with high efficiency for generating high pure hydrogen by hydrolysis in tap water of highly activated aluminum dross is established. Aluminum dross is activated by mechanically milling to particles of about 45 μm . This leads to removal of surface layer of the aluminum particles and creation of a fresh chemically active metal surface. In contact with water the hydrolysis reaction takes place and hydrogen is released. In this process a Zero Waste concept is achieved because the other product of reaction is aluminum oxide hydroxide (AlOOH), which is nature-friendly and can be used to make high quality refractory or calcium aluminate cement. For comparison we also used pure aluminum powder and alkaline tap water solution (NaOH, KOH) at a ratio similar to that of aluminum dross content. The rates of hydrogen generated in hydrolysis reaction of pure aluminum and aluminum dross have been found to be similar. As a result of the experimental setup, a hydrogen generator was designed and assembled. Hydrogen volume generated by hydrolysis reaction was measured. The experimental results obtained reveal that aluminum dross could be economically recycled by hydrolysis process with achieving zero hazardous aluminum dross waste and hydrogen generation.

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1. Introduction

Hydrogen energy is environment friendly. Because of the actual human ecology concerns, the exploitation of hydrogen as an universal fuel would be greatly supported. During the last two decades, the elaboration of the hydrogen based economy has made important progress an account of numerous researches such as the hydrogen fuel cell and the hydrogen cars [1–3]. Although these important discoveries constitute milestones toward a pollution free society, more research is needed to obtain the hydrogen easily and economically.

A convenient source of hydrogen is a reaction of aluminum with water to split the water molecules into hydrogen and oxygen. The hydrogen is released as a gas and the oxygen combines with the aluminum to form aluminum oxide compounds. Aluminum is the third most abundant element after oxygen and silicon in the earth's crust and constitutes approximately 8% by weight of the earth's crust. Aluminum is a safe material and is commonly used in the food, cosmetics and medical fields. Water is also abundant. Therefore, the reaction of these two elements to produce hydrogen represents an interesting proposal to replace fossil fuels [4–8].

To use pure aluminum in reaction with water to produce hydrogen is an expensive way. It is known that large amounts of

aluminum can be present as solid wastes. Using aluminum from this source to produce hydrogen has two impacts, one over the environment by recycling this waste and the second on the production cost. Aluminum from industrial solid waste comes in many forms with automobile production and food packaging being two of many possible sources. During aluminum melting dross is generated. Dross is classified into three different categories based on the metal content, i.e. white, black and salt cake. The main constituent of dross is aluminum metal, that varies from 8 to 80% depending upon grades [9]. Apart from aluminum metal, dross may also contain other compounds, e.g. Al_2O_3 , NaCl, KCl, CaO, NaAlCl_4 , KAlCl_4 , SiO_2 , MgO, etc. [10]. Waste from the production of aluminum comes in a variety of forms containing variable amounts of aluminum. The terms “white and black dross”, “salt cake”, “skim” and other designations refer to the amount of aluminum metal present and the morphology of the various wastes raked from the surface molten aluminum during processing and purification. While recognizing these distinctions, we refer to aluminum production waste collectively herein as dross. Worldwide the aluminum industry produces over 4.5 billion kilograms of aluminum production waste each year [11,12].

Indiscriminate disposal of aluminum dross in landfills can be problematic because landfills are not inert. Instead, a landfill is a complex active chemical reactor, so various reactions can be occurring during operation and closure. For example, aluminum waste can remain dormant for years in landfill but chemical reactions can develop when the buried aluminum comes into contact with

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alkaline water ($\text{pH} \geq 9$) that enters from a variety of sources. The resulting aluminum related chemical reactions are highly exothermic heat producing which can slow or stop desirable anaerobic microbial activity. Aluminum related reactions can also release large amounts of potentially toxic and/or flammable gases and noxious odors. The additional oxygen can lead to adverse reactions including combustion. These are a few reasons why aluminum dross is considered a hazardous material.

The aluminum dross is classified according to its metal content [12]. White dross may contain from 15 to 70% recoverable metallic aluminum. Black dross typically contains a mixture of aluminum oxides and slag, with recoverable aluminum content ranging between 12 and 18%, and much higher salt content (typically higher than 40%) than the white dross. The non-metallic residues generated from dross smelting operations is often termed 'salt cake' and contains 3–5% residual metallic aluminum [12]. Considering what is mentioned above the mixture from white, black dross and others compounds [13], can be used in reaction with water to produce hydrogen.

The main problem associated with the aluminum–water reaction is the existence of the hydroxide or oxide protective film on the aluminum particle surface, which does not dissolve in water and prevents the contact between the metal and water, hence slowing down (and practically avoiding) the chemical reaction between them [14–16].

Different methods to enhance the rate of aluminum reaction and other metals with water have been developed [17–20]. One of them suggests mechanical treatment of the metal (milling or cutting) which results in formation a fresh chemically active metal surface.

Others suggest melting or even evaporation of aluminum under water, typically by electric arc, to achieve fast reaction with water [21]. The use of aqueous alkaline solution, mainly with sodium hydroxide as a catalyst, was also proposed [22].

In this work, we have investigated the hydrolysis properties of Al powder and Al dross powder mechanically treated by ball milling to form a fresh chemically active metal surface. The aim is to accelerate the hydrolysis rate and to improve the hydrogen yields of the mixture in tap water at different water temperatures, including room temperature and different aluminum/water mass ratios. Continuous removal of the surface layer of aluminum particles by mechanical means sustains aluminum assisted water split reaction. Also, the presence of an effective amount of salts, especially KCl, NaCl, or oxides such as CaO in mixture 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 alkaline environment), which stimulates corrosion of Al with accompanying release of hydrogen. The activated aluminum can then react spontaneously with water, even room temperature without adding any chemicals to the water and hydrogen is generated.

2. Materials and methods

The starting materials used in experiments were: elemental powder of pure Al, size approximately $45 \mu\text{m}$ (99.5% purity) supplied by Alfa Aesar, a Johnson Matthey Company; Al dross powder with size between 100 and $300 \mu\text{m}$ supplied by S.C.AL Mina Com SRL, Bucharest, Romania; KOH, NaOH, >99.5% purity, supplied by Aldrich; nitrogen gas (N_2) with a purity of 99.99% purchased from Linde Company and tap water. Chemical composition of Al dross was determined by atomic absorption spectrometry method using an analyzer type Analytic Yena Nova 300 and this composition is presented in Table 1.

The pure Al powder was used as such and amounts of Na (from NaOH), K (from KOH), similar to the dross composition were used

Table 1
Composition of Al dross determined by atomic absorption method.

Component	Concentration (wt.%)
Al	43.3
Cr	0.088
Fe	4.32
Ca	0.45
Si	10.9
Na	0.8
K	0.21
Cu	1.17
Zn	0.9
Ni	0.87
Mg	1.85
Ti	0.27
Pb	0.053
Sn	–
Mn	0.2
B	–

in hydrolysis reaction. Al dross powder before use in experiments was ball milling and brought to about $45 \mu\text{m}$ size, using a Fritsch planetary ball mill with stainless steels balls and vials. Ball-to-powder mass ratio corresponds to 30:1, milling time was set in range 15–75 min and was sufficient to obtain Al dross particles size of about $45 \mu\text{m}$ and to get activated aluminum surface. The morphology of the powders was analyzed using scanning electron microscope JSM-7500 F (JOEL-Japan) operated at 10 kV.

The reactor was a 250 ml flat-bottomed glass flask (Fig. 1). The reaction was initiated by introducing of 100–200 ml alkaline tap water solution (obtained by dissolving 1.39 g NaOH and 0.302 g KOH respectively in 1000 ml of tap water) or tap water through the central vessel neck over 0.85–2.25 g of pure Al particles or over 1.96–5.20 g of Al dross particles respectively, poured in the flask from beforehand. After particles introduction, the neck of flask was immediately corked and before tap water solution or tap water introducing, all the system was flushed with N_2 gas for 5 min, to remove air from the system and to prevent formation of explosive mixture of hydrogen released in reaction with the air present in the reaction vessel. The temperature of the process was measured by a Chromel/Alumel thermocouple. To study the process in isothermal

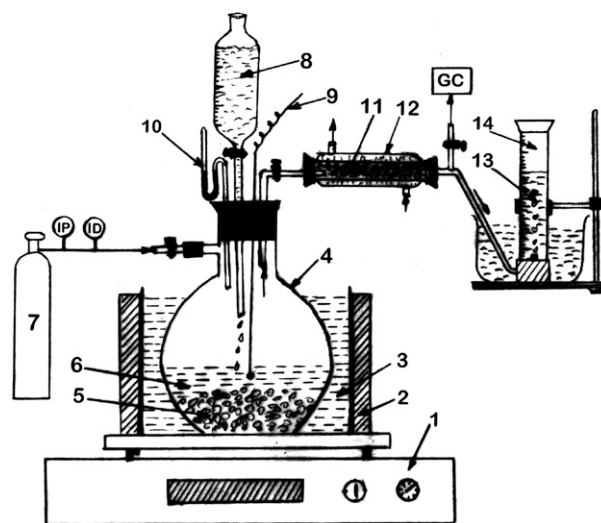


Fig. 1. Schematic experimental set up: (1) shaker; (2) heating tape; (3) water bath; (4) reactor vessel; (5) Al powder or Al dross powder; (6) alkaline tap water solution or tap water; (7) cylinder containing nitrogen under pressure; (8) burette with alkaline tap water solution or tap water; (9) thermocouple; (10) pressure gauge; (11) dryer; (12) condenser; (13) gas burette graduated in 0.1 ml increments at room temperature filled with deionized water for hydrogen gas collecting; (14) hydrogen volume collected; (GC) gas chromatograph; (IP) pressure indicator; (ID) flowmeter.

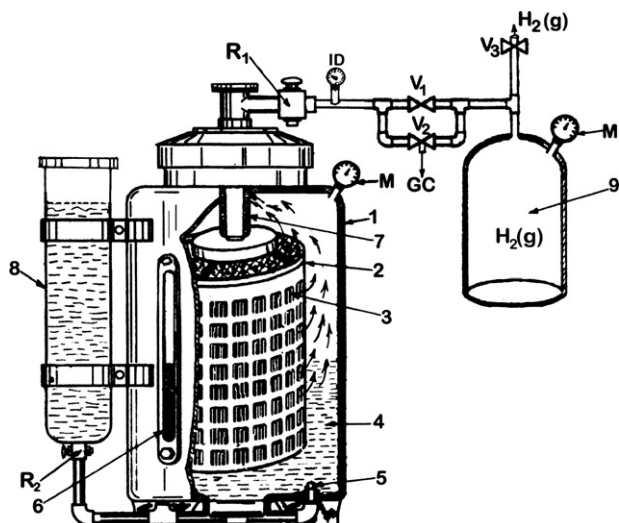


Fig. 2. A schematic representation of hydrogen generator: (1) recipient; (2) fuel cartridge (Al dross powder); (3) perforated basket to support the fuel cartridge; (4) tap water; (5) nozzles; (6) sight glass; (7) vertical tube to sustain the fuel cartridge with a series of holes therein for admitting the hydrogen gas; (8) water bottle with a piping system; (9) gas tank; M – manometer; R₁, R₂ – taps; V₁, V₂, V₃ – valves; GC – gas chromatograph; ID – flowmeter.

conditions, the glass reactor was placed in a water bath, filled with water preheated to the desirable temperature.

The gas produced was flowed through a condenser and dryer to remove all water vapors before measurement of hydrogen (H₂) volume. The H₂ volume was measured by the water trap method and corrected to a gas volume at standard temperature and pressure (STP). Atmospheric pressure on that day was obtained from local weather office. These experiments were carried out at a temperature of 21 °C and an atmospheric pressure of 758 mm of Hg. The tube inserted into neck through cork ensures the directing of hydrogen gas through water into an inverted 1000 ml burette. The hydrogen gas released has displaced the water in the burette, and the changing water level in the burette was measured as a function of time. The rate of change of the water level provided an indication of the rate of hydrogen generation from the reaction, and the difference between the initial and final water levels in the burette has indicated the total hydrogen yield.

At regular intervals gas samples were taken using a gas tight syringe (1 ml), to measure the H₂ purity released from the reaction. The H₂ purity was determined by gas chromatography method using a chromatograph type Hewlett Packard 5890 A, equipped with packed stainless steel Porapak-Q column and molecular sieve

5A packed column, with a flame ionization and conductivity detectors and helium carrier.

Two different experimental setups were employed for the study of hydrolysis reaction and hydrogen generation when the aluminum comes in contact with tap water. First setup (involving the experimental system from Fig. 1), was used to gain comparative data on the amount of hydrogen released by reaction between pure Al powder and alkaline tap water solution or Al dross powder and tap water respectively. The influence of different parameters on the aluminum/water reaction rate, e.g. milling time, aluminum/water mass ratio, temperature was studied in the experiments.

As a result of the original setup, a hydrogen generator was designed and assembled to evaluate hydrogen volume generated in the reaction of mechanically milled aluminum dross with tap water. Generator scheme is shown in Fig. 2.

A fuel measure (2) is preferably comprised of a perforated basket (3) lined the inside with felt and filled with aluminum dross powder. The felt prevents aluminum particles to pass through holes of basket and ensures a continuous absorption of water of the fuel unit (2) and also hydrogen leakage released from hydrolysis reaction through holes.

3. Results and discussion

3.1. Mechanical treatment of aluminum dross

The main problem associated with the aluminum–water reaction is the existence of the hydroxide or oxide protective film on the aluminum particle surface, which does not dissolve in water and prevents the contact between the metal and water, hence slowing down (and practically avoiding) the chemical reaction between them [14–16]. Different methods to enhance the rate of aluminum reaction with water have been developed. One of them suggests mechanical treatment of the metal (milling or cutting) which results in formation of a fresh chemically active metal surface [17–20].

Large quantity of materials can be treated using a planetary ball mill (Fritsch Pulverisette), which employs strong centrifuge forces to create high-energy milling actions inside the container such as shown in Fig. 3a. Fig. 3b and c shows the photos of Al dross before and after milling process.

Because a large number (30) of the balls are used and the container rotates at a high speed of 500 rpm, the milling frequency is very high. A short milling time of 60 min is thus needed to get particle size of 45 μm with chemically active surface. The experimental results show that ball milling (BM) has played an essential role in the formation of the Al particles with fresh surface. During the BM, material particles are repeatedly flattened, fractured

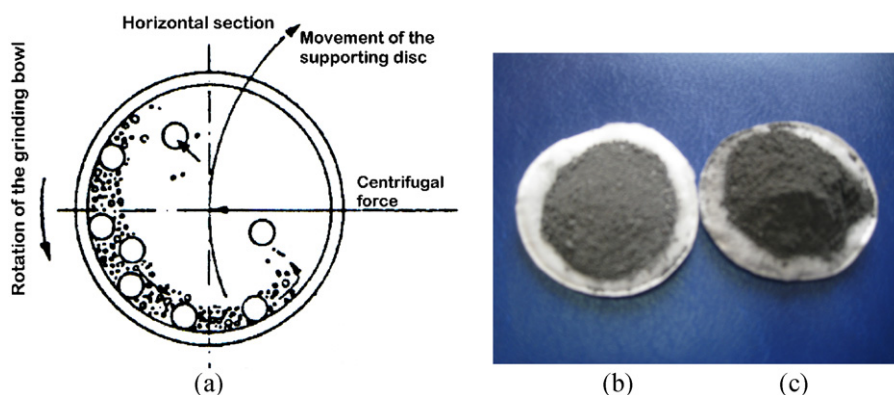


Fig. 3. Schema of a planetary ball mill (a) and photos with Al dross: before milling (b) and after milling (c).



Fig. 4. Regular (left) and activated (right) aluminum dross powders in tap water at room temperature, the regular aluminum dross powder shows no apparent reaction, whereas the activated aluminum exhibits effervescent reaction with hydrogen release.

and welded. Every time two steel balls collide or one ball hits the chamber wall, they trap some particles between their surfaces. The high-energy impacts severely deform the particles and create atomically fresh, new surfaces, as well as a high density of dislocations and other structural defects. Such a high defect density can accelerate the diffusion process. Furthermore, the deformation and fracturing of particles cause continuous size reduction and lead to reduction in diffusion distances. This can at least reduce the reaction temperatures significantly, even if the reactions do not occur at room temperature. The detailed BM role on the formation of a fresh chemically active metal surface could be in the creation of a precursor containing nucleation structures. Ball milling of Al powder dross at room temperature produces a disordered and nanoporous structure through agglomeration of micro-sized particles under ball impacts. Mechanical activation by BM produces smaller grain size, possibly higher surface area and disordered structure, which should all contribute a reduced reaction temperature and a higher chemical reactivity in comparison with samples without the milling treatment. The specific surface area of aluminum dross before milling was measured by BET method with Macsorb HM analyzer, Model-1201, manufactured by Mountech Co., Ltd., and the aluminum dross powder had a BET specific surface area of $0.6 \text{ m}^2/\text{g}$. After milling for 60 min, the specific surface area of aluminum dross powder was $3.4 \text{ m}^2/\text{g}$. As shown from the data obtained by mechanical grinding the surface area was increased and aluminum particle surface activated. So the key to induce and maintain the reaction of aluminum with water at room temperature is the removal and/or disruption of the hydrated alumina layer. The activated aluminum can then react spontaneously with water even at room temperature and at neutral pH without adding any chemicals to the water.

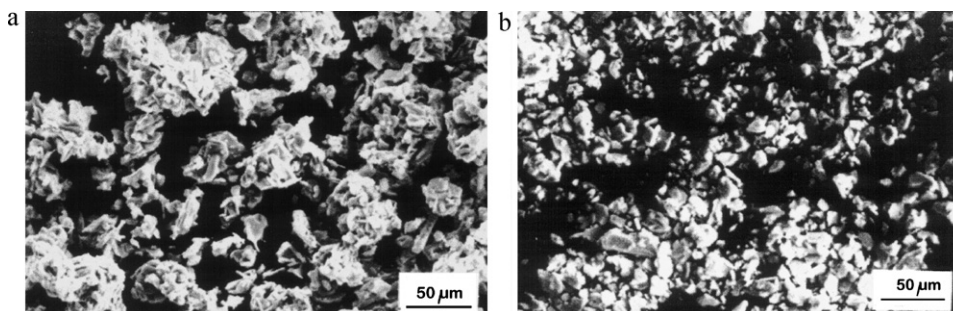


Fig. 5. Scanning electron microscopy (SEM) images of Al dross samples before and after milling: (a) without milling; (b) for the sample milled for 60 min.

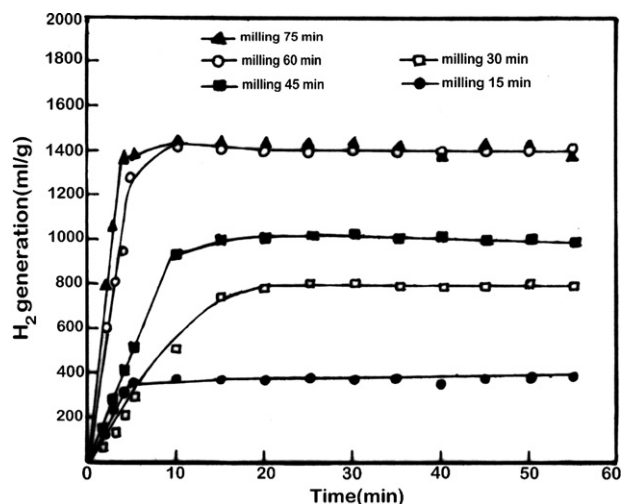


Fig. 6. Hydrogen generation in hydrolysis of 1 g of Al from dross in 100 ml tap water at different milling time and temperature of 21°C .

The reactivity of Al dross powder and hydrogen released of the non-activated and activated aluminum is presented in Fig. 4, showing the evolution of hydrogen bubbles, in contrast, as received aluminum dross powder, which does not react with tap water.

Fig. 5a, shows the SEM image of the starting Al dross sample without ball milling. This sample contains particles of different sizes/shapes (Fig. 5a)

SEM image of Al dross sample milled for 60 min (Fig. 5b) shows particles of smaller size, but unsystematic shapes. From this figure it is seen that through dross milling with a planetary ball mill (PBM) results particles of smaller size. The major role of the ball milling is to fracture the particles and to reduce the size, a longer milling time can help to activate and complete the structural changes which are crucial to the desired chemical reactions.

Milling time has some effects on the Al particles reactivity. This is confirmed in Fig. 6, which presents the hydrolysis rates of Al particles from dross powder in tap water as a function of milling time.

The hydrolysis rate and hydrogen generation of Al dross powders are increased with the increase of milling time, and the hydrolysis efficiency reaches maximum for 60 min milling, then the hydrolysis rate and hydrogen generation remain almost constantly. The improvement of Al dross powder reactivity is partly resulted from the decrease of the particles size and activating aluminum particles surface.

3.2. Hydrolysis reaction of aluminum dross with tap water

The experiments were carried out to demonstrate that under certain conditions Al dross powder, after mechanical treatment

Table 2

Hydrogen volume released during the reaction of different amounts of pure aluminum powder (size 45 μm) with 100 ml tap water solution (solution obtained by dissolving 1.39 g NaOH and 0.302 g KOH respectively in 1000 ml of tap water), at 21 °C and an atmospheric pressure of 758 mm of Hg.

No. sample	Al (g)	H ₂ (l)	H ₂ (l) STP	H ₂ (l) theoretical	Yield (%)	Time (s)
1	2.25	3.18	2.93	2.80	104.64	285
2	2.20	3.11	2.87	2.74	104.74	279
3	2.05	2.90	2.67	2.55	104.70	260
4	2.10	2.82	2.60	2.62	99.24	253
5	1.54	2.12	1.95	1.92	101.56	190
6	1.43	1.98	1.82	1.78	102.25	177
7	0.98	1.35	1.25	1.22	102.45	121
8	0.85	1.17	1.08	1.06	101.88	105
A (average)	1.68	2.33	2.15	2.09	102.68	209

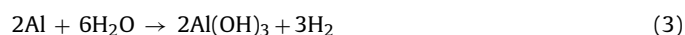
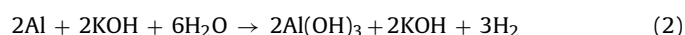
Table 3

Hydrogen volume released during the reaction of different amounts of aluminum dross powder (size about 45 μm) with 100 ml of tap water, at 21 °C and an atmospheric pressure of 758 mm of Hg and a milling time of 60 min.

No. sample	Al dross (g)	Al (g)	H ₂ (l)	H ₂ (l) STP	H ₂ (l) theoretical	Yield (%)	Time (s)
1	5.20	2.25	3.22	2.98	2.80	106.43	290
2	5.08	2.20	3.14	2.91	2.74	106.20	284
3	4.73	2.05	2.93	2.71	2.55	106.35	266
4	4.85	2.10	2.95	2.73	2.62	104.15	258
5	3.56	1.54	2.15	1.99	1.92	103.64	195
6	3.31	1.43	2.03	1.88	1.78	105.61	183
7	2.26	0.98	1.39	1.29	1.22	105.73	126
8	1.96	0.85	1.20	1.11	1.06	104.71	109
A (average)	3.87	1.68	2.38	2.20	2.09	105.53	214

through ball milling, react with tap water and from process the hydrogen is generated. In the experiments without mechanical treatment of the metal the reaction does not start. In all experiments with mechanical treatment of the metal the reaction started in a few seconds and continued for a few minutes, until depletion of the aluminum particles. It was noticed that a typical reaction with less 3 g of aluminum, is complete in less than 5 min. The results of these experiments are shown in Tables 2 and 3.

The Al particles reacted with aqueous solution of sodium and potassium hydroxide to produce hydrogen gas at temperatures near room temperature. The corrected volume of gas produced was compared to the theoretical quantity of hydrogen gas, which is obtained according to Eqs. (1), (2) or (3). In this process, a Zero Waste concept is achieved because the other product of reaction is aluminum oxide hydroxide (AlOOH), according to Eq. (4), which is nature-friendly and can be used to make high quality refractory or calcium aluminate cement [13].



The content of NaOH and KOH from tap water solution play the role of catalysts for the reaction between aluminum and water.

As it can be seen in Fig. 7, aluminum particles react with water at the surface (2) of the alkaline solution and defines at and near the surface a region of substantial effervescence (see also Fig. 4).

This region represents the reaction zone (RZ). The height of the reaction zone varies with the intensity of the reaction and extends above and below the surface of the alkaline solution. During the reaction a precipitate (3) accumulates between Al particles at the bottom of the reaction vessel. From experimental tests is indicated to maintain the reaction zone at a height (H) of at least about 10 mm above the precipitate, to prevent as the precipitate to mix with aluminum particles into the reaction zone.

The hydrogen generation rate was calculated from the amount evolved from the beginning of the test. Hydrogen production is expressed as yield (%) defined as the volume of produced hydrogen

corrected to a gas volume at standard temperature and pressure (STP), over the theoretical volume of hydrogen that should be released, assuming that all material is hydrolyzed. The first, second and third reactions form the aluminum hydroxide $[\text{Al}(\text{OH})_3]$ and hydrogen, according to Eqs. (1), (2) and (3). Then the aluminum hydroxide $[\text{Al}(\text{OH})_3]$ can transform in aluminum oxide hydroxide (AlOOH), according to Eq. (4). All (1)–(3) reactions are thermodynamically favorable from room temperature past the melting point of aluminum (660 °C) [23]. All reactions are also highly exothermic [23,24].

The results from Tables 1 and 2 show that the reaction is reproducible and produces stoichiometric quantities of hydrogen gas. The 102.68 and 105.53 average yield of hydrogen gas for pure aluminum powder and aluminum dross powder respectively are considered to be within the measurement uncertainty. However, there are at least two factors which might have contributed to a slightly higher

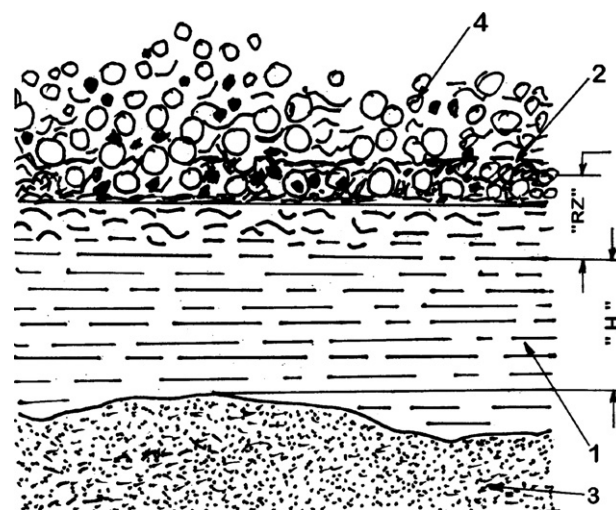
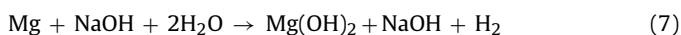
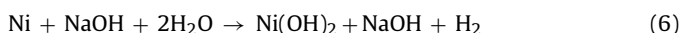
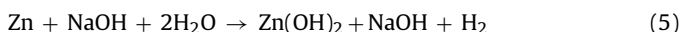


Fig. 7. Schematic representation of reaction zones for the reaction between Al and water in the reaction vessel from Fig. 1: (1) alkaline solution; (2) effervescence surface of alkaline solution; (3) Al particles and precipitate; (4) foam; RZ – reaction zone; H – height between precipitate and RZ.

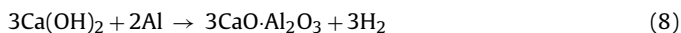
Table 4
Purity of hydrogen released from reaction of Al with water for the experiments presented in Tables 2 and 3.

No. sample	Gas analysis			
	Gas from pure Al powder		Gas from aluminum dross powder	
	Hydrogen (vol.%)	Nitrogen (vol.%)	Hydrogen (vol.%)	Nitrogen (vol.%)
1	98.88	Balance	98.82	Balance
2	98.96	Balance	98.65	Balance
3	97.68	Balance	98.42	Balance
4	99.25	Balance	97.74	Balance
5	98.95	Balance	99.68	Balance
6	97.92	Balance	98.04	Balance
7	98.75	Balance	98.56	Balance
8	99.14	Balance	98.41	Balance
A (Average)	98.69	Balance	98.54	Balance

hydrogen yield. Firstly, the volume of gas produced was corrected to STP. It is possible that the exhausted fume hood in which the experiments were carried out could have lowered the reaction pressure below the atmospheric pressure of 758 mm of Hg. This would have increased the observed value for the volume of gas produced. An exhaust bench typically runs at 25.4–50.8 mm of water pressure. At a maximum, this could have increased the measured volume by about 0.5%. Secondly, the water used was tap water in all cases, in which dissolved air may have been present. If any of this air had been released in the presence of the warm hydrogen gas, this would have increased the volume of the gas measured. This would have affected the results by less than 1%. As it can be seen the average production of hydrogen gas is greater when using aluminum dross powder than when using pure aluminum powder. This can be explained by the fact that in dross composition other metals are present (Table 1), which in alkali medium can also generate hydrogen (i.e., Zn, Ni, Mg, etc.) in accord with Eqs. (5), (6) and (7):



The content of Na, K, Ca from aluminum dross once contacted with water cause substantial increase of pH (i.e. create high alkaline environment, a pH value measured of us in experiments was 10.37), which stimulates corrosion of Al with accompanying release of hydrogen, according to Eqs. (1), (2) and (8):



Produced calcium hydroxide is reacted with aluminum to produce calcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) and hydrogen. Samples of gas for each experiments from Tables 2 and 3 were obtained and analyzed. The results are presented in Table 4.

The data from Table 4 show that the purity of the hydrogen collected in all samples was high, the concentration average of hydrogen released from reaction of pure aluminum with alkaline tap water solution was of 98.69 vol.%. The concentration average released from reaction of aluminum dross powder with tap water was similar of 98.54 vol.%. This is close to what was theoretically expected. The lower value of 97 vol.% H_2 concentration obtained

Table 5
Start and final temperature in the system for all experiments from Tables 2 and 3.

Sample	Temp. average for the system pure Al/water				Temp. average for the system Al dross/water			
	Temp. (°C)		Bath		Temp. (°C)		Bath	
	Reactor start	Reactor finish	Start	Finish	Reactor start	Reactor finish	Start	Finish
1–8	21.2	45.6	20.3	24.27	21.2	46.05	20.3	24.3

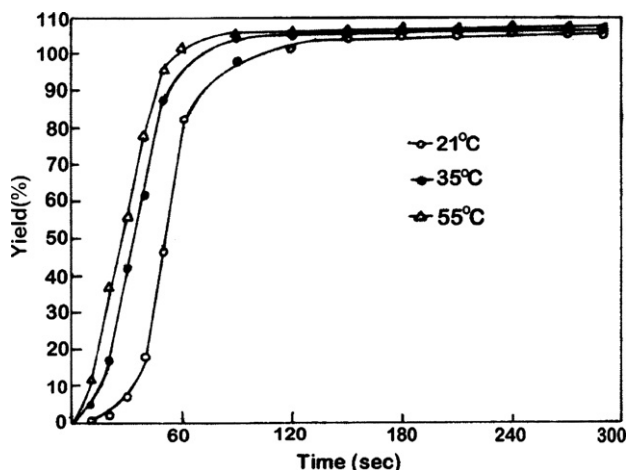


Fig. 8. Effect of initial temperature of water (100 ml) on hydrogen generation rate of aluminum dross powder containing 2.25 g Al, milled 60 min.

in three samples was probably due to the fact the system was not completely purged with hydrogen before the samples were taken.

The temperature of alkaline tap water solution and tap water was measured before and after the reaction, and at about 5 min after the reaction was completed. The results are summarized in Table 5. All reactions are highly exothermic, the heat of the reaction could be evaluated.

Fig. 8 presents hydrogen generation rate of Al dross powder milled for 60 min, after being poured in 100 ml tap water at different initial temperature. As one can see, increasing the temperature of water leads to an important increase in hydrogen generation rate.

The exothermic nature of the aluminum water reaction generates heat (see Table 5), that will be employed to increase the temperature of water, and which will in general increase reaction rates. To do this, minimum amount of water must be used in process and in this case, water temperature will increase as the reaction progresses, needing no external heat source for the reaction to be accelerated.

Fig. 9 shows the effect of amount of water at initial temperature of 21 °C on its temperature variations when reacts with Al dross powder containing 2.25 g Al, milled for 60 min.

As illustrated in this figure, the temperature of water increases while decreasing its amount. To benefit from above mentioned advantage, in hydrogen generator (from Fig. 2), 100 ml of tap water to 5.20 g Al dross powder (2.25 g Al, see Table 3) was used.

To check if all aluminum amount has reacted with water the solid resultant product after the hydrolysis reaction was dried at 110 °C for 6 h and milled once again for 1 h in the planetary mill, maintaining the ratio ball-to-powder mass of 30:1. Then this powder was checked for the hydrogen evolution following the similar hydrolysis conditions presented in Section 2.

After a contact time of 12 h between water and powder milled and maintaining water temperature at 55 °C in the system from Fig. 1, there was no released of a significant volume of gas that can be measured. In addition, the gas chromatographic analysis of gas samples taken from system has indicated a gas composition of 99.75 vol.% nitrogen (flushed gas) and under 0.25 vol.% hydrogen. These data support the hypothesis that almost the entire amount of

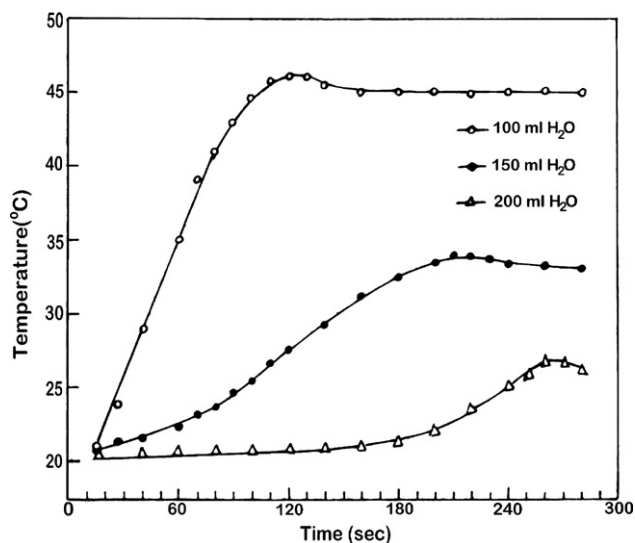


Fig. 9. Effect of amount of water at initial temperature of 21 °C on its temperature variations when reacts with Al dross powder containing 2.25 g Al, milled 60 min.

aluminum present in dross powder has initially reacted with water and hydrogen gas was generated. Even in the situation where a small amount of aluminum is still present in the solid residue produced, its use in the production of refractory material requires a process of calcination at high temperature >900 °C [25,26], which determines the conversion of aluminum to aluminum oxide, a product safe for the environment and people.

3.3. Hydrogen generator

Based on experimental data, a hydrogen generator was designed and assembled and the hydrogen quantity generated in the reaction of mechanically milled aluminum dross for 60 min with tap water was evaluated. The capacity of this generator is of about 500 g of Al dross powder, which contains about 216.5 g Al. The initial temperature was 21 °C. The generator has worked continuously 8 h at a hydrogen generation rate of about 0.667 l/min. The purity of hydrogen generated was 98.5 vol.%. In accord with the hydrolysis reaction, represented by Eq. (3), the amount of hydrogen calculated is 269.42 l (STP). The volume of hydrogen measured was of 282 l (STP). This confirms that other metals present in the composition of aluminum dross (see Table 1) generate hydrogen by hydrolysis reactions according to Eqs. (5)–(8). Fig. 10 shows the evolution of hydrogen flow rate generated with system presented in Fig. 2.

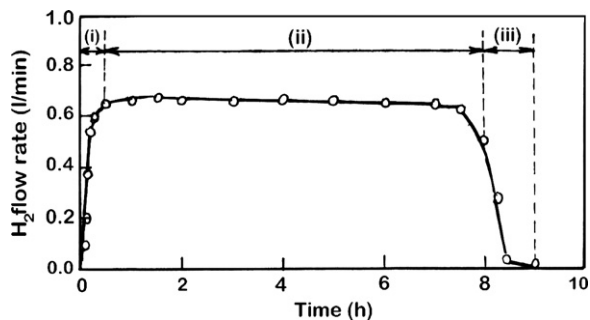


Fig. 10. Evolution of hydrogen flow rate generated in the reaction between aluminum dross powder and tap water using the system from Fig. 2, with the three distinct areas: (i) the entrance in optimal operating mode; (ii) operation optimum hydrogen production; (iii) aluminum depletion filter corresponding to fairly rapid decrease of the hydrogen flow generated.

Reporting the results to time, the generation of hydrogen at a concentration of 98.5 vol.% takes about 8 h. After this time the hydrogen flow rate drops sharply, which shows that the entire amount of Al in the slag was completely exhausted. A confirmation of the operation flow generator is on the evolution of hydrogen generated, which was measured and is represented by the curve in Fig. 10. From this figure it can see three distinct areas: (i) the entrance in optimal operating mode; (ii) operation optimum hydrogen production at a rate of 0.667 l/min; (iii) the amount of aluminum depletion filter, corresponding to fairly rapid decrease of the flow of hydrogen released. These results show clearly that Al dross can be successfully used for generating high purity hydrogen.

3.4. The analysis of the resultant products to highlight achieving of zero hazardous waste

Zero Waste is a strategic vision of a community. It supposes that raw materials in the system will be recycled, and will not end in an incinerator or in landfills. At first sight the idea that it will not produce any waste may seem as a utopian dream. However, in fact this is an attainable aim, and an increasing number of towns, municipalities and companies all over the world are gradually joining this movement. In the very beginning it is necessary to come true that the term Zero Waste does not mean reduction of production of all waste to zero – this is not possible in a society oriented on consumption. The term means elimination of the present way of waste disposal by depositing to landfills and incineration. Selection of this aim is important, because it does not present a choice. We must do anything possible in order to achieve it. The Zero Waste vision requires a change in our way of thinking and of established practices. Instead of solving the problem of what to do with the produced waste, we must concentrate, especially, on the issue of how to manage natural resources more wisely, and how to reduce the total volume and hazardousness of waste. In the first place, it is necessary to prevent waste creation, secondly, to reduce its amount and toxicity, and, thirdly, it is necessary to repair products. If these steps are not possible, then recycling is required.

Aluminum dross is the residual waste material produced during an aluminum melting process, and it poses a risk to people and the environment. When it is deposited and stored in landfills, dross is hazardous to the environment by generating undesirable heat, liquid leachate with heavy metals, toxic and smelling bad gases such as hydrogen sulfide, carbon monoxide, ammonia. Recycling of this hazardous material and its converting into value-added products, clean for environment such as the hydrogen and aluminum oxide hydroxide (AlOOH), as has been presented in this paper, is in agreement with the achieving of the Zero Waste concept. Both products resulted by aluminum dross hydrolysis reaction are environmentally friendly.

The hydrogen is considered a clean fuel that has a minimum impact on the environment nearly eliminating the levels of carbon dioxide and other greenhouse gas emissions. In its molecular form, as result by aluminum dross hydrolysis reaction, the hydrogen can be used directly as a fuel to drive a vehicle, or indirectly to produce electricity for industrial, transport and domestic use. The huge advantage that hydrogen has over other fuels is that as a fuel it is non-polluting, because the only emission from its combustion is water. Hydrogen also is a nearly ideal fuel in terms of smog reduction when is combusted. Hydrogen does not contain carbon or sulfur, so no CO, CO₂ or SO_x or soot are producing during combustion. Hydrogen in a fuel cell produces zero harmful emissions. Oxides of nitrogen are completely eliminated due to the low operating temperatures (~80 °C) of the cells. Hydrogen is non-toxic, so uncombusted hydrogen does not pose a direct health risk.

Aluminum oxide hydroxide (AlOOH), is known as the boehmite or pseudoboehmite. While the boehmite is an oxyhydroxide of

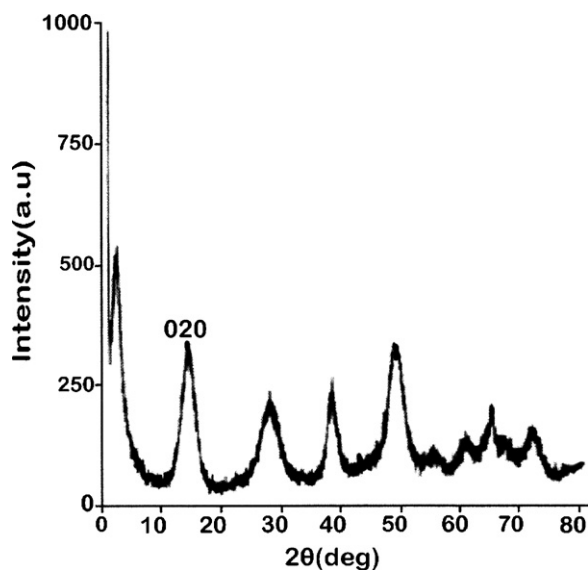


Fig. 11. XRD curve of a solid residue sample resulted from aluminum dross hydrolysis reaction, showing the line broadening and lower intensities of pseudoboehmite, especially of the 020 reflexion.

aluminum (composition, AlOOH or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) that always occurs in nature as microcrystals or nanocrystals, the pseudoboehmite (composition, AlOOH) is synthetic pure (pseudocrystallized) aluminum hydroxide gel and its XRD pattern is similar to that of boehmite but with the differences in the relative intensities of the peaks, all boehmite reflexions are present, including the basal reflexion ($d_{(020)}$). The value ($d_{(020)}$) = 6.11 Å = 0.611 nm must be met [27]. From aluminum dross hydrolysis reaction this form must appear. The XRD curve of solid residue sample resulted from aluminum dross hydrolysis reaction is presented in Fig. 11 and this curve shows the line broadening and intensities, especially of the 020 reflexion.

This means that the XRD curve of this sample meets the above mentioned criteria and highlights pseudoboehmite formation in the hydrolysis reaction. X-ray diffraction analysis was made using a Philips PW 1710 diffractometer with Ni filter and Cu α radiation. Also the SEM analysis (see Fig. 12) of the dried hydrolyzed powder highlights the formation of aluminum oxide hydroxide (AlOOH) and the aluminum dross absence.

It can be seen from SEM image, the hydrated surface show the morphology that is characteristic for boehmite/pseudoboehmite product (composition AlOOH) and corresponds to the data presented in literature [27]. The SEM micrograph shows needle type

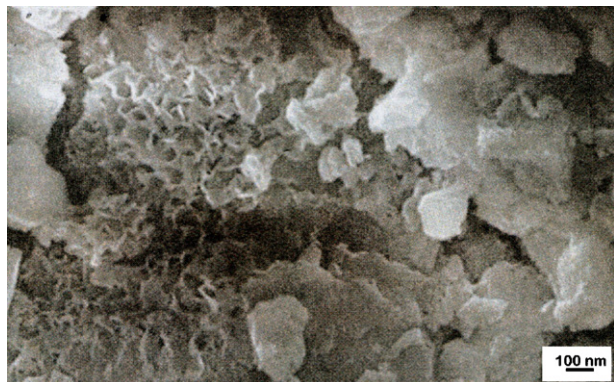


Fig. 12. SEM image of the AlOOH product resulted after hydrolysis reaction of the aluminum dross, at 55 °C, grain size < 100 nm, low crystallinity.

structures with size ranges in the nanometer scale, these structures are characteristic for AlOOH product. All the results support the idea that almost the entire aluminum amount that is present in dross powder has initially reacted with water and solid residual product of reaction is aluminum oxide hydroxide (AlOOH), which is nature-friendly and can be used to make high quality refractory or calcium aluminate cement.

4. Conclusions

This work presents an investigation of hydrogen generation by the reaction of mechanically milled aluminum dross with tap water. Experiments conducted in isothermal conditions, with measurement of the quantity of hydrogen released and temperature of the process, have shown that a fast, self sustained reaction of activated Al dross with tap water takes place even at room temperature and can result in about 100% hydrogen yield. Depending of parameters such as mass ratio of Al dross and tap water, milling duration, reaction temperature, a great improvement of hydrolysis reactivity for Al dross powder was observed. The results indicate that the Al dross powder has a high hydrogen yield and hydrolysis rate. The improvement of reactivity for Al dross is explained by its treating by ball milling to form a fresh chemically active metal surface and the decrease of particle size. The 60 min milled Al dross have fast hydrolysis rate and can produce high hydrogen yield. The experimental results obtained reveal that aluminum dross could be economical recycled by a hydrolysis process with achieving of promising systems for hydrogen generation and zero hazardous aluminum dross waste.

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