

**UNIVERSITY OF GAZIANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES**

**HYDROGEN GAS GENERATION FROM WATER BY USE OF
ALUMINUM DROSS**

**M. Sc. THESIS
IN
MECHANICAL ENGINEERING**

**BY
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M.Sc. in Mechanical Engineering

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**Hydrogen Gas Generation from Water by Use of
Aluminum Dross**

M.Sc. Thesis

in

**Mechanical Engineering
University of Gaziantep**

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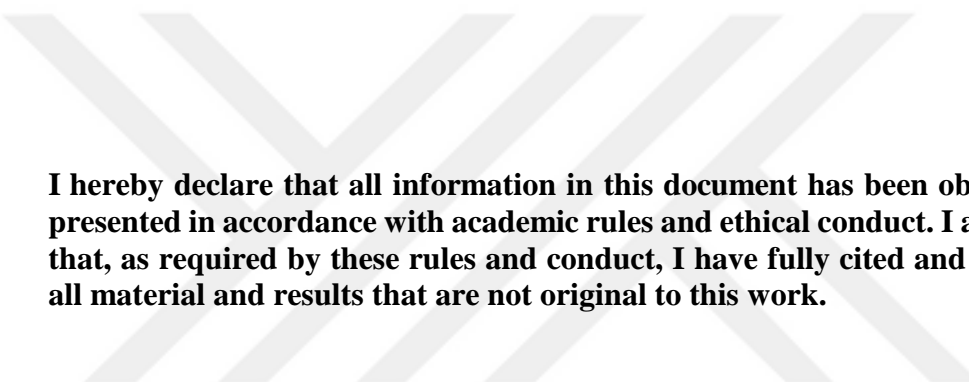
by

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August 2017



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ABSTRACT

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In this thesis, hydrogen gas was generated in a reactor from the chemical reaction of water and aluminum dross which is a waste of aluminum production plants and aluminum die casting factories. An experimental setup consisting of a reactor, control and measurement devices has been constructed on Gaziantep University Campus to perform these reactions. This experimental setup has been tested with many experiments under different operating conditions to investigate the technical feasibility and efficiency of producing hydrogen gas. In addition, the amount of generated hydrogen gas, its heating value and the amount of heat released due to the exothermic reaction in the gas mixture were measured by using Gas Chromatography and Gas Calorimeter. At the end of the experiments, 120 L of hydrogen gas was produced after reacting 2 L of hot tap water at 100°C with 1 kilogram of aluminum dross. However, the amount of hydrogen in the gas mixture by gas chromatography was measured in 93,243% purity, and the heating value of the gas mixture by gas calorimeter was measured as 2375 kcal/m³.

Keywords: Hydrogen gas, reactor, aluminum dross, heating value, gas chromatography

ÖZET

ALÜMİNYUM CÜRUFU KULLANARAK SUDAN HİDROJEN ÜRETİMİ

KALE, MEHMET

Yüksek Lisans Tezi, Makine Müh. Bölümü

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Bu tezde, alüminyum üretim tesislerinin ve alüminyum döküm fabrikalarının bir atığı olan alüminyum cürufu ve suyun kimyasal reaksiyonundan bir reaktör içerisinde hidrojen gazı üretildi. Bu reaksiyonları gerçekleştirmek için Gaziantep Üniversitesi Kampüsü'nde bir reaktör, kontrol ve ölçüm cihazlarından oluşan bir deney düzeneği kurulmuştur. Bu deneysel kurulum, hidrojen gazı üretiminin teknik fizibilitesini ve verimliliğini araştırmak amacıyla farklı çalışma koşulları altında çok sayıda deneyle test edilmiştir. Buna ek olarak, üretilen hidrojen gazı miktarı, ısı değeri ve gaz karışımı içinde ekzotermik reaksiyona bağlı olarak açığa çıkan ısı miktarı Gaz Kromatografisi ve Gaz Kalorimetresi kullanılarak ölçülmüştür. Deneylerin sonunda, 100°C'de 2 L sıcak musluk suyu ile 1 kilogram alüminyum cürufunun reaksiyonundan sonra 120 L hidrojen gazı üretildi. Bununla birlikte, gaz kromatografisi ile gaz karışımındaki hidrojen miktarı %93,243 saflıkta ölçülmüş ve gaz karışımının ısı değeri gaz kalorimetresi ile 2375 kcal/m³ olarak ölçülmüştür.

Anahtar Kelimeler: Hidrojen gazı, reaktör, alüminyum cürufu, ısı değeri, gaz kromatografisi



To My Parents

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NOMENCLATURE

D	diameter, cm
H	height, cm
L	liter, dm ³
LHV	low heating value, kcal/m ³ - kcal/kg
P	pressure, atm
T	temperature, °C - K
T _{water}	initial water temperature, °C
V	volume, L
W	weight, kg
ΔG	the change in Gibbs free energy, kj/mol
ΔH	enthalpy change, kj/mol
ΔS	entropy change, J/K

Subscripts

Al	aluminum
bar	a metric unit of pressure
BD	black dross
GC	gas chromatography
h	hour
H ₂	hydrogen
HPR	hydrogen production reactor
kg	kilogram
kWh	kilowatt hour
min	minute
NDE	negative difference effect
Ph	potential of hydrogen
TDC	thermal conductivity detector

UBCs	used beverage cans
U.S.	United States
V	volt
α alumina	xz-L14 nano alumina is white fluffy pow



CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Our world faces one of the most serious problems of traditional energy sources that are depleting, such as fossil fuels (petroleum, coal and natural gas). When these fuels are consumed, it will affect the quality of life in the worst way by causing environmental pollution such as global warming, air pollution, climate change and acid rain. In order to solve the energy problem, scientists have been looking for alternative fuels that do not pollute the environment. Hydrogen (H_2) is a clean form of energy that does not pollute nature when burned, and so it is the most investigated source of energy by scientists. The interest in hydrogen is increasing day by day, because it is a clean energy source, the lightest fuel, the most abundant element in the universe, and it is the fuel that gives the highest energy per unit mass in all known storable and transport fuels [1].

Hydrogen is the most basic and lightest element in the world, consisting of only one electron and one proton [2]. It does not exist as an element alone in nature, but in the form of compounds such as water which constitutes 80% of the world and hydrocarbons which is in the contents of fuels. Hydrogen gas has three times more energy efficiency than petroleum and it has a great potential to solve fuel needs of the planet. Hydrogen was first seen as an alternative energy source at the end of the 1960s [3], and this interest has begun to increase since 1990s [4].

The concept of hydrogen economy envisions that hydrogen fuel will be used instead of fossil fuels in order to satisfy the need of the world's energy in the near future [5]. Excessive dependency on fossil fuels has threatened energy supply security of

countries, especially which don't have any proven fossil resources. Recently, hydrogen has emerged not only environmentally but also economically as an alternative fuel. In the future, when the transition to the hydrogen economy increases, the developments related to hydrogen production must be completed [6]. Hydrogen is predicted to be the most ideal fuel of the future for many uses areas, e.g. it can generate electricity, used in fuel cells (fields of application: automobiles, buses, space technology, planes, locomotives, ships, submarines, portable power sources), hydrogen powered industries, space shuttle and rockets, in fusion processes and for all our domestic energy requirements. Hydrogen powered fuel cells and hydrogen-fueled internal combustion engines are predicted to be new technologies of the future, primarily due to its clean burning [7–10]. Nowadays, hydrogen-fueled vehicles have begun to be produced, and therefore, many major automobile companies are in competition with each other to produce a commercial hydrogen-fueled car. Hydrogen is already used as preferred fuel for space research. When an international space station is built in the future, it will be used as fuel in space transportation, at the same time to provide electricity and portable water for its environment.

Hydrogen can be produced from fossil fuels by restructuring the natural gas with steam, by gasification of the coal, by partial oxidation, through electrolysis, e.g. from renewable energy and in nuclear reactors by processes such as water electrolysis, water photoelectrolysis [11]. Hydrogen is used in a wide range of applications. According to a research conducted in 2007, approximately 50 million tons of hydrogen has been used in various industrial establishments such as synthesis of ammonia, chemical processes, and refining processes [12]. 96% of hydrogen production is provided from fossil fuels (50% from natural gas, 30% from crude oil, 20% from coal). The remaining 4% is produced by electrolysis [13], but all of these methods are very expensive. The greatest advantage of energy obtained from hydrogen is that it has zero carbon emissions, because as a result of the use of hydrogen in fuel cells or as a result of combustion processes, only water occurs [14].

Fossil fuels are the biggest source of distress, because they cause air pollution and are quickly consumed. For this reason, researchers should be directed to finding suitable alternative solutions for energy carriers that will be used in energy-producing or energy-consuming areas. Above all, hydrogen has proven to be a clean energy

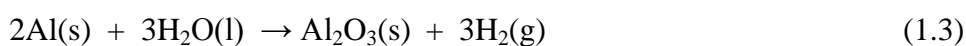
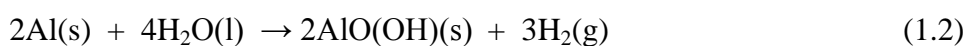
source and energy carrier with high calorific value [15,16]. Water is the highest source in terms of hydrogen potential because i) the water contains hydrogen at high level (111 kg/m³), and ii) as a result of combustion of hydrogen in fuel cell, water is obtained [17].

Chemical reactions of some metal reactants generate hydrogen as their product. Aluminum, its alloys and wastes are regarded as one of the most basic sources for future hydrogen production, and especially in recent years, studies are being made to obtain energy using aluminum and the likes. In addition, the use of metals for hydrogen production is defined as being more reliable for energy storage, more efficient, easier to use, causing less pollution than other hydrogen production methods.

Hydrogen generation due to the reaction of some metals with water was first proposed in the late 19th century [18]. In 1972, Smith et al. [19] described an approach using an amalgamated aluminum surface for the production of hydrogen gas. In a US patent received by Gutbier and Hohne in 1976 indicated that hydrogen could be produced through the reaction of magnesium-aluminum mixtures with sea water [20]. Since that time, the production of hydrogen by the reaction of water with aluminum-based metals has been the subject of many papers and patents. All of the aluminum-based researches propose information to overcome the aluminum oxide protective layer, so that aluminum can continue to react with water.

Even though the reaction of aluminum and water is thermodynamically favorable, it does not proceed due to the presence of the alumina oxide layer which acts like a thin wall on the surface of aluminum metal and prevents the water from directly contacting the aluminum metal underneath it [21].

Eqs. (1.1, 1.2 and 1.3) shows the possible reactions which can occur between aluminum and water [21].



In Eq. (1.1), aluminum hydroxide gibbsite Al(OH)_3 and hydrogen are formed, in Eq. (1.2) aluminum hydroxide boehmit AlO(OH) and hydrogen are formed, and in Eq. (1.3) aluminum oxide and hydrogen are formed. From room temperature to the melting point of aluminum (660°C), all of these equations are thermodynamically favorable and they are all quite exothermic. Among the aluminum hydroxides, Al(OH)_3 is the most stable component from room temperature to 280°C , and AlO(OH) is the most stable component from 280°C to 480°C . Above 480°C , Al_2O_3 becomes the most stable compound [22]. Appendix A shows more detailed thermodynamic properties of the aluminum-water reaction.

Table 1.1 Thermodynamics of the aluminum-water reaction

$2/3\text{Al(s)} + \text{H}_2\text{O(l)} = 2/3\text{Al(OH)}_3\text{(s)} + \text{H}_2\text{(g)}$			
T, °C	ΔH , kJ/mol H_2	ΔS , J/K	ΔG , kJ/mol H_2
0	-277	26,2	-284
100	-284	3,29	-285
200	-291	-12,1	-285

The ΔG values of the aluminum-water reaction shown in Table 1.1 indicate that aluminum must spontaneously react with water. On the other hand, a piece of aluminum put into water under room temperature conditions does not react with water in practice. The reason is that aluminum has a thin, regular and adherent of aluminum oxide layer (Al_2O_3) on the surface of it, and this layer prevents the reaction with water. Therefore, in order for the reaction of aluminum with water to occur continuously at room temperature, the hydrated aluminum oxide layer must be dissolved, removed and/or disrupted during the reaction. Some organizations that support the development of aluminum-water reactions for the production of hydrogen are shown in Appendix B [21].

Many researchers have made observations on the formation of hydrogen in aluminum corrosion reactions. Therefore, they focused their studies on using aluminum for the hydrogen production. Pure aluminum is a highly reactive metal, so

it is sensitive to corrosion with ion forms. Dissimilar from other metals, according to some theories the electrochemical corrosion of aluminum-based materials cannot be predicted using the Wagner-Traud mixed potential model due to existence of the negative difference effect (NDE). In other words, the hydrogen evolution rate will increase with increasing anodic polarization [23]. The basic reasons behind the NDE facts have not been completely understood yet. Aluminum and its alloys have strong attraction with oxygen and so that a dense oxide layer is formed on the surfaces. Because their surfaces are well protected, this situation shifts the corrosion potential of aluminum by nearly 1 V in the positive direction. Therefore, it is known that aluminum based materials are generally well resistant to corrosion. Such a resistance can be a great advantage for aluminum use in construction materials; however, this resistance becomes the major obstacle to continuous hydrogen production through aluminum corrosion. Aluminum corrosion processes are completely CO₂-free and by-products have minimal environmental impact [6].

Aluminum is not found in nature as an element alone [24]. Aluminum metal and its alloys have an extremely wide range of uses, which means a high demand for aluminum [25]. Nowadays, there are two different ways to produce aluminum; primary aluminum production is produced from bauxite ore, secondary aluminum production is produced from recycled products (from aluminum scraps or places using aluminum products). In 1990, total aluminum production was 28 million tonnes, of which more than 8 million tonnes were recycled from scraps, and total aluminum production in 2010 was about 56 million tonnes, of which about 18 million tonnes were recycled from scraps. It is predicted that in 2020 the metal demand in the world will increase to 97 million tons and that 31 million tons of scrap metal will be recycled [26]. In the primary aluminum production process; first, 2 tons of alumina (Al₂O₃) is obtained from 4 tons of bauxite ore and 2 tons of red mud waste is occurred as a by-product. And then 1 ton of aluminum is produced from 2 tons of alumina. The first smelting operation requires 17,000 kWh of power to produce 1 ton of aluminum in primary aluminum production whereas the second operation requires only 750 kWh (only 4.4% of that used for initial smelting). For this reason, the aluminum produced from recycled materials leads to a lower environmental pollution than the primary aluminum [27]. However, the amount of waste metal that can be recycled is quite large [28]. The main source in secondary aluminum production is scrap aluminum. The most commonly

used aluminum scrap resources are beverage canisters, commercial scrap, folio, process scrap, sawdust, extrusions, and old rolled or cast metal [29].

Approximately 20 to 35 kg of aluminum dross is produced from each 1 ton of liquid aluminum production [27]. The primary aluminum dross contains approximately 70 - 80 wt. % metallic aluminum, and this proportion is in the range of 5 wt. % to 10 wt. % metallic aluminum for the secondary aluminum dross. Primary aluminum dross can be recovered because it contains high amounts of metallic aluminum, but secondary aluminum dross is usually stored in solid waste storage areas because it contains low amounts of metallic aluminum [30].

In addition to hydrogen production, the reaction between water and aluminum results in aluminum oxide hydroxide and/or aluminum hydroxide precipitates which are environmentally friendly and have many industrial applications such as water treatment, alumina production, flame retardant, paper manufacturing, fire prevention and so on [17,31]. Therefore, the idea of producing hydrogen by corroding aluminum in water becomes an attractive option.

1.2 Aim and objectives

The aim of this study was to accelerate the hydrolysis rate of the aluminum dross in tap water by using different reaction temperatures, pressures, and different aluminum dross/water mass ratios. The mass percent of hydrogen in the gas mixture and its calorific value were determined. Also, amount of heat released during the exothermic reaction of aluminum dross and water was determined. Therefore, heat provided by the reaction can be effectively utilized in other application areas. The experiments have been carried out in a closed reactor. The steady tests of the reactor array have been performed under the variations of inlet pressure, inlet temperature and aluminum dross/water mass ratios.

1.3 Outline of the thesis

This thesis is composed of five chapters beginning with an introductory chapter.

Chapter 2 gives a literature review about the modeling and experimental studies for hydrogen production with aluminum/water reaction. It concentrates on chemical reactions developed for the system in order to analyze its performance parameters under different operating conditions.

Chapter 3 provides materials and experimental techniques for this thesis.

Chapter 4 presents the effects of temperature and pressure on experimental results under different conditions which are tested in this study. Also, gas chromatography results and calorific values are presented.

Chapter 5 shows the overall conclusions obtained by the results from each chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There is a very high energy consumption in the aluminum production process and a large amount of dross is produced as a waste product during aluminum smelting or refining [32]. Aluminum dross is formed on the surface of molten Al that is exposed to furnace atmosphere during primary and secondary Al fusion processing. Al dross is a mixture of free metallic aluminum and nonmetallic substances such as aluminum oxide, carbide, nitrite, salts and metal oxides [33]. The main components of the aluminum dross are Al_2O_3 , CaO, MgO with small amounts of Si and Fe [34]. In aluminum production plants or aluminum die casting factories, metallic aluminum is directly oxidized and converted to aluminum oxides during aluminum production process. Then, the dross is taken out and cage-like structures is formed by the formation of dross with oxide film. These structures take small aluminum particles inside and imprison them so that they cause the loss of aluminum metal. At the end of this process, three different dross types are formed. These are called white dross, black dross and salt cake. White dross has a very large amount of metal content (15 to 70 wt. %) and a lower amount of oxide and salt, and also it has a structure of large clumps or blocks. Black dross (BD) has a small amount of metal content (12-18 wt. %) and more oxide and salt, and also has a granular structure such as sand. On the other hand, nonmetallic waste from dross melting process is termed salt cake. It contains oxides, carbides and sulphides and has a lower metal content (3 to 5 wt. %) [32]. The dross with less than 20 wt. % Al content is very difficult to be recycled and so it is stored [35]. When it is stored and deposited in these areas, the dross is poisonous and it causes emission of harmful gases such as ammonia, hydrogen sulfide, carbon monoxide and also generates undesirable heat, contaminates the groundwater by liquid leachate with

heavy metal [36]. This dangerous waste caused by the aluminum industry poses a huge threat and problem to human life, plants and animals due to environmental pollution [24,37].

Unfortunately, there is no efficient and economical technique to reduce the environmental pollution of stored and discarded slags so far. In many studies, it has been discussed how aluminum dross can be useful for recycling and re-use. In most studies, it is mentioned that high temperature processes are applied during the recycling of dross. Ewais et al. [38] used different ratios of aluminum dross, aluminum sludge and alumina sinters to manufacture calcium aluminate cement which can be used to produce fire-resistant bricks. In further studies, dross was used to manufacture hexagonal mesoporous aluminophosphate [39]. Hong et al. [40] passed recycled aluminum through an electric arc furnace and submerged it to manufacture an Al-Si alloy and brown fused alumina. Yoshimura et al. [41] used an electrical plasma furnace to make the dross useful. Aluminum was recovered and used as a new additive material for manufacturing refractory materials. In addition, various researchers have used mixed dross and zircon to produce mullite/zirconia composites using different furnace times and temperatures [42].

The production of aluminum is primarily energy intensive process. Furthermore, most of the research has remained in the laboratory environment or only in the article phase. For this reason, a large amount of dross is produced as a waste product during the remelting or refining of aluminum. Storage, disposal, destruction and relocation of aluminum dross waste is a major problem for all countries in the world. There are millions of tons of dross waste, and the amount of this waste is increasing every year depending on the aluminum industry.

The molten aluminum in the furnace is covered with molten salt flux which provides a protective function between the metal and the atmosphere and allows the metal to accumulate and separate easily. The nonmetallic components from the raw mix are completely absorbed by the liquid flux. Before the molten metal is trapped, the top layer, a dark-colored material called BD, is tapped or removed by skimming. Each year, 95% of BD is landfilled in the world [43]. Depending on the market price of aluminum and the cost of transportation, BD can be processed to recover

approximately 20% of the remaining metal by means of salt bath rotary furnaces or hammer mills, which physically separate aluminum from the dross. When the recovery of aluminum from dross is not economically justifiable, it is disposed of in landfills [44,45].

Due to the characteristics of hazardous wastes according to European catalog, the BD is classified as toxic and hazardous waste (100309) [46]. It is admitted as “highly flammable” (H3-A: substances and preparations which, in contact with water or moist air, produce highly flammable gases in dangerous quantities), "Irritant" (H4: non-corrosive substances or preparations that cause inflammation of the skin or mucus membrane in the immediate, prolonged or repeated contact), "Harmful" (H5: substances and preparations with limited health risk when they are inhaled, swallowed or when they are penetrated the skin), and “leachable” (H13: Substances and preparations capable by any means, after disposal, of yielding another substance) [46,47]. The main problem is its leachability (H13), and its high reactivity with water or even with moisture in the air (H3-A) which leads to the formation of poisonous, explosive, harmful, toxic and unpleasant odorous gases, such as H_2 , H_2S , NH_3 , PH_3 , CH_4 , etc. Consequently, when BD is stored in hazardous waste storage, pollution of ground water (e.g. Cl^- , F^- , CN^- , NH_4^+ , high pH conditions) and ambient air (e.g. NH_3 , CH_4 , H_2) can be observed [47–54].

In recent years, lawmakers of many countries have imposed strict regulations on air pollution and on the disposal of various industrial wastes in order to improve the quality of the environment. In addition, waste disposal costs (operational cost) is very high, because it requires special landfills. Nowadays, the increasing environmental regulations have forced the secondary aluminum industries around the world to consider recycling technologies about the reduction of waste [55,56].

Alternative processes have also been proposed for BD treatment, in order to recover aluminum in various forms. In this context, obtaining hydrogen from aluminum dross+water mixture could be promising for the future and this could offer an interesting alternative for BD recycling [43].

At the end of the chemical reaction of aluminum and water, hydrogen gas is generated. Hydroxide ions (OH^-) in water-soluble bases can dissolve AlO_2^- which is a thin oxide layer on the aluminum surface. For this reason, aluminum and its alloys are reacted with water even at room temperature in the alkaline solutions and cause production of hydrogen. Among the different bases, sodium hydroxide (NaOH) is the most commonly used base. However, using this method to obtain the hydrogen gas is too expensive because of the requirements of the use of the various catalysts in the reaction [6].

In this study, recycling of this hazardous material and converting into valuable products which are not harmful to the environment such as hydrogen (H_2) gas, aluminum oxide hydroxide ($\text{AlO}(\text{OH})$), aluminum hydroxide ($\text{Al}(\text{OH})_3$) have been presented. Therefore, this study aims to achieve the Zero Waste concept. All of the valuable products resulted by aluminum dross hydrolysis reaction are environmentally friendly [36].

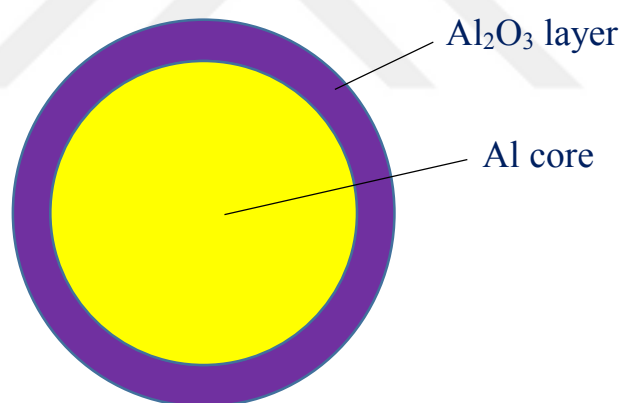


Figure 2.1 Aluminum oxide layer around aluminum core

Aluminum metal is very reactive and its surface is instantly coated with a nano-thick layer composed of Al_2O_3 and thus, it will not be reactive between pH 5 and 9. As shown in Figure 2.1 aluminum oxide layer around the Al core prevents elemental Al entering the reaction with water.

Aluminum dross generally includes several oxide compounds such as; CaO , Na_2O , K_2O . These compounds react with water to form the strong alkaline solution during the reaction. This alkaline solution dissolves the aluminum oxide layer around the

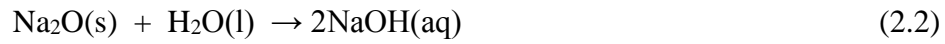
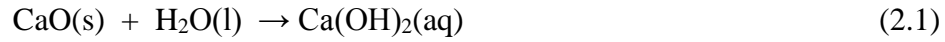
aluminum core. Thus, aluminum core is exposed for reaction with water in alkaline conditions. As a result, aluminum core reacts both with water and bases to generate hydrogen gas. Chemical composition of Al dross was determined by using an atomic absorption spectrometry (Rigaku ZSX Prims II) and results are presented in Table 2.1. XRF analysis results performed in ÜSKİM laboratory are shown in Appendix C.

Table 2.1 Composition of Al dross

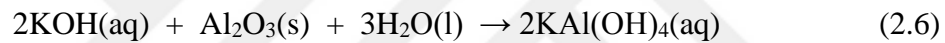
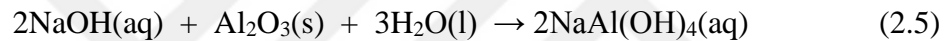
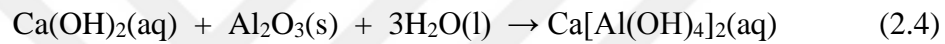
Formula	Concentration	Element	Concentration
Al ₂ O ₃	52,91%	Al	41,96%
CaO	12,47%	Ca	18,30%
SiO ₂	7,61%	Si	6,24%
MgO	7,41%	Mg	6,16%
Cl	4,26%	Cl	8,02%
TiO ₂	3,64%	Ti	4,92%
SO ₃	3,42%	S	2,51%
Na ₂ O	2,42%	Na	1,92%
BaO	1,67%	Ba	3,29%
Fe ₂ O ₃	1,63%	Fe	2,72%
K ₂ O	1,07%	K	1,76%
P ₂ O ₅	0,60%	P	0,48%
ZnO	0,32%	Zn	0,64%
CuO	0,16%	Cu	0,30%
PbO	0,11%	Pb	0,25%
MnO	0,07%	Mn	0,13%
NiO	0,07%	Ni	0,13%
SrO	0,05%	Sr	0,11%
Cr ₂ O ₃	0,06%	Cr	0,10%
V ₂ O ₅	0,04%	V	0,04%
MoO ₃	63 PPM	Mo	0,01%
Br	55 PPM	Br	0,01%
Ga ₂ O ₃	57 PPM	Ga	99 PPM
ZrO ₂	52 PPM	Zr	67 PPM
CoO	27 PPM	Co	31 PPM

2.2 Chemical reaction formulas in the process of hydrogen formation

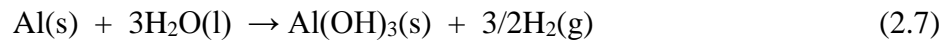
1-First, strong bases form by the reaction of metal oxides and water according to Eq. 2.1 [57,58], 2.2 [58], 2.3 [59],



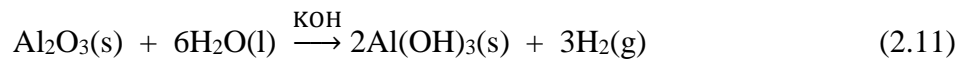
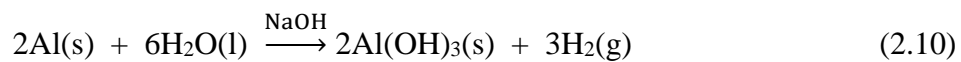
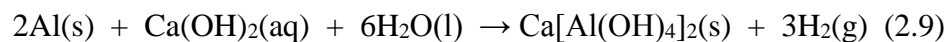
2-These strong bases dissolve the aluminum oxide layer around the aluminum core according to Eq. 2.4 [57], 2.5 [60], Eq. 2.6 [57,61]:



3-Al core reacts with water to generate hydrogen according to Eq. 2.7, 2.8, additionally, the zero waste products of the reactions, (AlO(OH) and 2Al(OH)₃), are obtained.



4-Also, Al core reacts with water under alkaline conditions to generate hydrogen gas according to Eq. 2.9 [57], Eq. 2.10 and 2.11 [36]:



In this study, neither any catalyst nor any additive material were used while obtaining hydrogen gas. In addition, optimization and reduction of energy costs by using a reactor has been carried out by using a reactor. This method has been known as economical and also due to the disposal of hazardous waste, it has been studied more than other methods. At the end of the experiments, a flammable gas mixture was obtained. A large portion of the gas mixture was determined to be hydrogen gas.



CHAPTER 3

EXPERIMENTAL SETUP

3.1 Hydrogen production reactor (HPR)

3.1.1 System description

The system is called Hydrogen Production Reactor (HPR) which is shown in Figure 3.1, and it is composed of a reactor and a condenser. These two components are linked with a closed circuit which is called a pipe.



Figure 3.1 The HPR setup

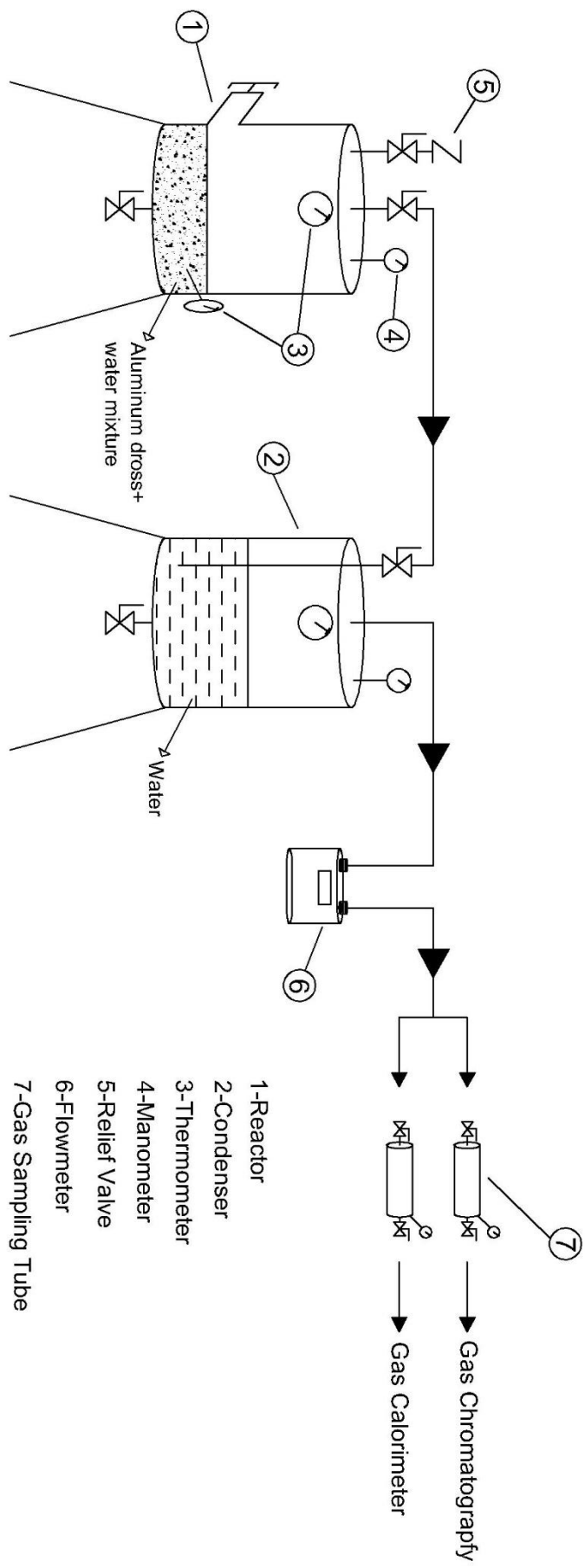


Figure 3.2 Schematic diagram of the HPR setup

Schematic diagram of the HPR set up is shown Figure 3.2. Table 3.1 gives the technical properties of the reactor, the condenser and the gas sampling tubes used in this study.

Table 3.1 The dimensions and technical properties of the HPR components

Material	Height(cm)	Diameter(cm)	Volume(L)	Type
Reactor	44	21	15	steel
Condenser	44	21	15	steel
Tube	22	7,8	1	steel

3.2 System components

3.2.1 Reactor

The reactor is a closed pressure vessel, and is made of steel. The reaction of aluminum dross and water takes place immediately after they are mixed inside the reactor.



Figure 3.3 Reactor

3.2.2 Condenser

The condenser which has a similar shape like the reactor is also closed and it is a pressurized vessel made of steel. The condenser was filled with water and it helps to

condense the water vapor (steam) inside as the hot gas mixture comes out of the reactor. Thus, purer form of hydrogen gas can be obtained.



Figure 3.4 Condenser

3.2.3 Thermometer

At the top and the bottom of the reactor, there exists two thermometers (Badotherm 200°C-sized). Temperature of the dross and water mixture were measured by the thermometer attached to the bottom of the reactor and temperature of the gas mixture was measured by the thermometer attached to the top of the reactor.



Figure 3.5 Thermometer

3.2.4 Manometer

At the top of the reactor there exists one manometer (Badotherm 10 bar-sized) to measure the pressure of the gas mixture.



Figure 3.6 Manometer

3.2.5 Relief valve

It is mounted on top of the reactor for safety purposes.



Figure 3.7 Relief Valve

3.2.6 Flowmeter

Volume of hydrogen gas is measured by a flowmeter (Itron G4 type) which is mounted to the condenser outlet.



Figure 3.8 Flowmeter

3.2.7 Gas sampling tube

In the same way, two pressure-resistant gas sampling tubes made of steel were used to collect the gas samples.



Figure 3.9 Gas sampling tube

Black dross used in this study was supplied by Zahit Aluminum Factory (Figure 3.4). Many experiments have been made with different amounts of aluminum dross and tap water.



Figure 3.10 The sample of aluminum dross

These experiments were performed under two different conditions: atmospheric pressure and pressurized conditions. In addition to mixing the aluminum dross with the tap water at room temperature, aluminum dross was mixed with tap water which is heated to elevated temperatures prior to mixing in order to determine the effect of reaction temperature on the reaction rate. The hydrogen purity was determined by using a gas chromatography (Hewlett Packard 5890 A). The calorific value of the gas mixture was measured using a gas calorimeter (Yokogawa Model CM6G).

CHAPTER 4

RESULTS and DISCUSSIONS

4.1 Introduction

In this chapter, the effect of temperature and pressure on accelerating the hydrolysis rate of the system is examined. And also the test results obtained from the experimental studies have been analyzed. The chromatographic and heating values of the gas mixture obtained at the end of the reaction are presented.

4.2 Effect of temperature

The amount of generated hydrogen at different initial temperatures of water is presented in Figure 4.1.

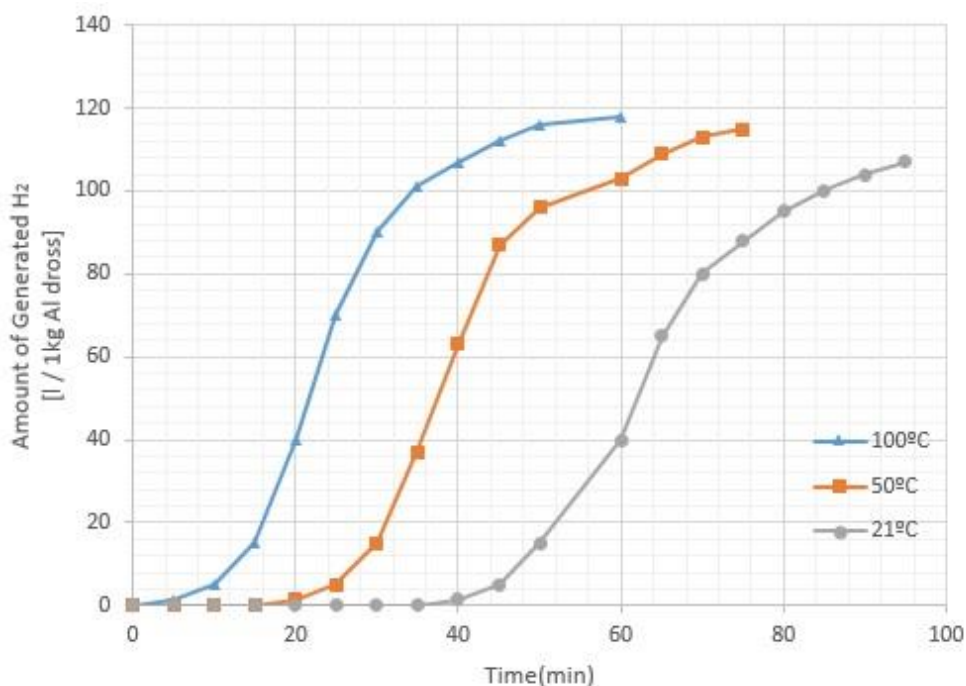


Figure 4.1 Effect of initial temperature of water on hydrogen generation rate of reaction mixture containing 1 kg aluminum dross and 2 L tap water.

It can be seen that with increasing initial temperatures of water, hydrogen generation rate increases whereas the induction time decreases. The reaction of Al dross with water progresses very slowly in cool water ($T_{\text{water}}=21^{\circ}\text{C}$), with an increasing rate at moderate temperature ($T_{\text{water}}=50^{\circ}\text{C}$) and at an even faster rate at the highest temperature ($T_{\text{water}}=100^{\circ}\text{C}$) tested in this study. The average amount of hydrogen gas generated was determined to be ~ 120 L from the reaction of 1 kg of Al dross with 2 L of tap water at a temperature of 100°C .

4.3 Effect of pressure

The amounts of hydrogen gas generated at two different pressures as a function of time are illustrated in Figure 4.2. Both reactions were carried out by reacting Al dross with hot tap water ($T_{\text{water}}=100^{\circ}\text{C}$). At $P=1$ atm, the average amount of hydrogen gas generated was determined to be ~ 65 L measured by the flowmeter at 35 mins after the reaction started and the generation of H_2 gas was diminished 80 mins after the reaction started. At this point, the average amount of hydrogen gas generated was determined

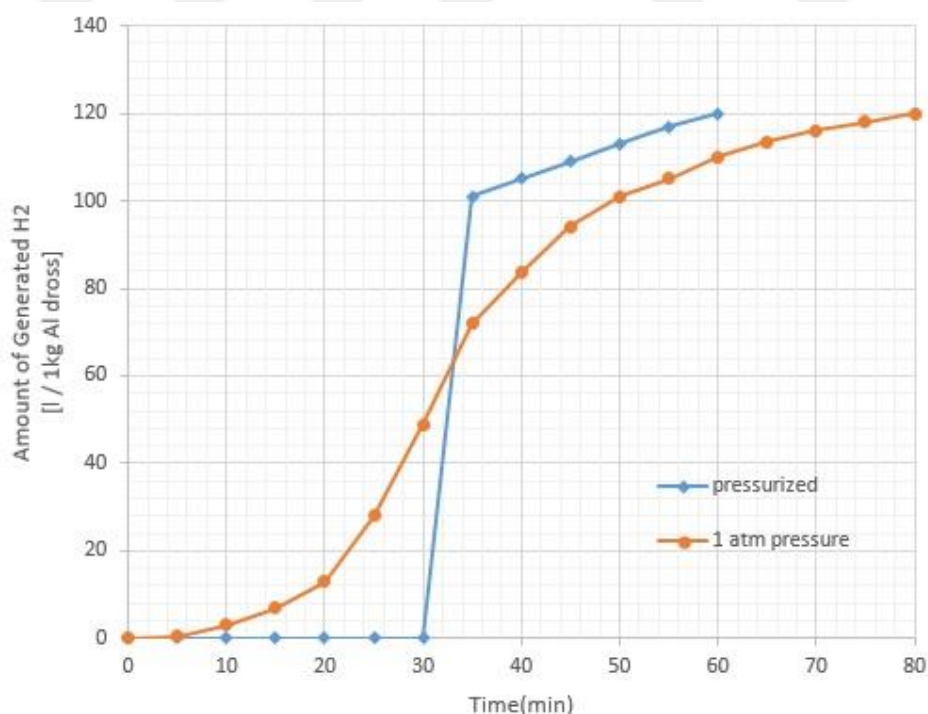


Figure 4.2 The amount of hydrogen generated versus time at different pressures for the reaction mixture containing 1 kg Al dross and 2 L water at $T=100^{\circ}\text{C}$

to be ~120 L. While conducting the experiment under the pressurized condition, the reactor's valve was kept closed until 35 mins after the reaction started and so that the pressure of the gas mixture continuously increased. When pressure of the gas mixture reached to ~6 bar, the valve was opened. Immediately after opening the valve, the amount of hydrogen gas generated was measured to be 102 L measured by the flowmeter.

The generation of H₂ gas was diminished 60 mins after the reaction started or 25 mins after opening the valve. At the end of the reaction, the average amount of hydrogen gas generated was determined to be ~120 L. which has the same value that of the reaction conducted at P=1 atm. Clearly, hydrogen generation rate increased at pressurized condition compared to atmospheric pressure condition. Conducting reaction at pressurized conditions will increase the hydrogen gas generation rate at a continuous system in a large facilities.

4.4 Generation of pressurized hydrogen

Figure 4.3 shows the change in the temperature and the pressure of the reaction

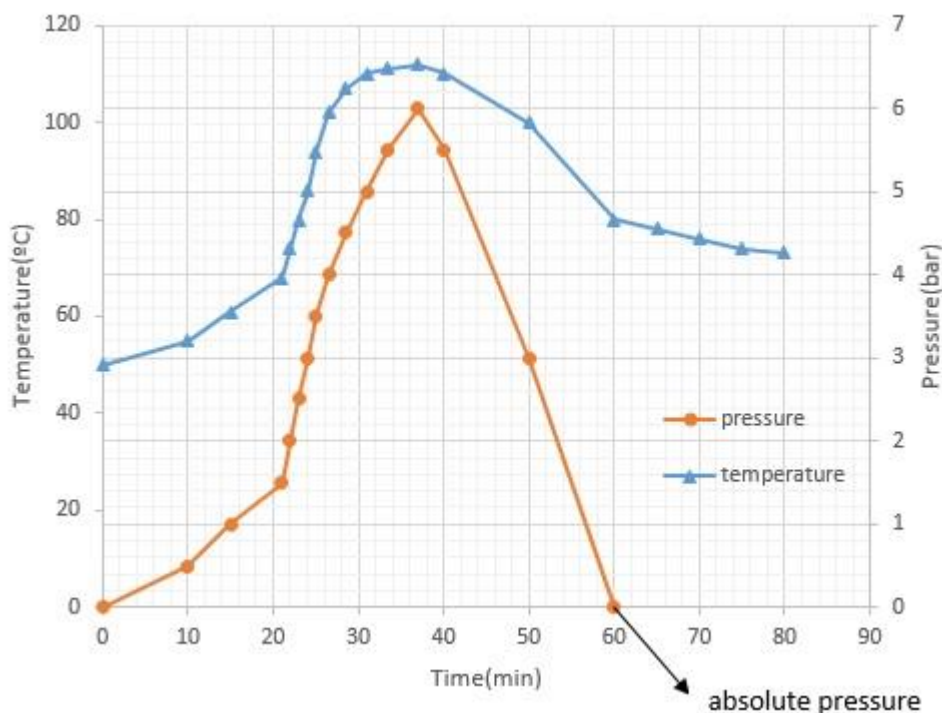


Figure 4.3 Variation of the temperature and pressure in the closed reactor

mixture with respect to time as the reaction is started under atmospheric pressure conditions. The temperature increased step by step with the increase of the pressure. In the end, when the temperature reached to 112°C, the pressure reached to ~6 bar and the safety valve became functional. After reaching a maximum at ~35 min, both temperature and pressure gradually decreased. These results show that the reaction of hydrogen generation is definitely not limited by pressure under the experimental conditions. This reaction is spontaneous and any form of energy is not needed to start the reaction. When Al dross/water mass ratio is being increased in the reaction mixture, it was observed that both temperature and pressure rise.

If large plants based on this study are developed in the future, higher pressures and temperatures can be obtained while generating hydrogen gas without any spent energy. In addition, if the hydrogen gas is used in places closer to the hydrogen generation plant, the transportation of hydrogen gas can be carried out by using the plant's generated pressure and hence the high-pressure hydrogen production process appears to be an important means for the purification and storage of hydrogen [63].

4.5 Chromatography values

At the end of the experiment, gas mixture sample was taken for GC analysis and its parameters of gas mixtures are shown in Appendix D. Figure 4.4 shows both the GC spectrum of pure hydrogen gas as a reference and GC spectrum of the gas mixture obtained from the reaction of Al dross with water.

As can be seen from the spectrum of the gas mixture, peak associated with hydrogen gas is clearly visible. This confirms that hydrogen generation resulted from the reaction of Al dross with water. The amount of H₂ gas in the gas mixture was found to be as 93,243 wt. %.

According to the GC results, gases other than H₂ that were determined in the gas mixture and as shown in Figures (4.5-4.7) are SO₂, (4,125 wt. %), N₂ (2,181 wt. %), O₂ (0,230 wt. %), CO₂, CH₄ and C₁-C₆ hydrocarbons (0,221 wt. %). If these gases are let pass through various membrane filters or purification processes, all the unwanted gases can be removed. In this way, higher purity hydrogen gas can be obtained.

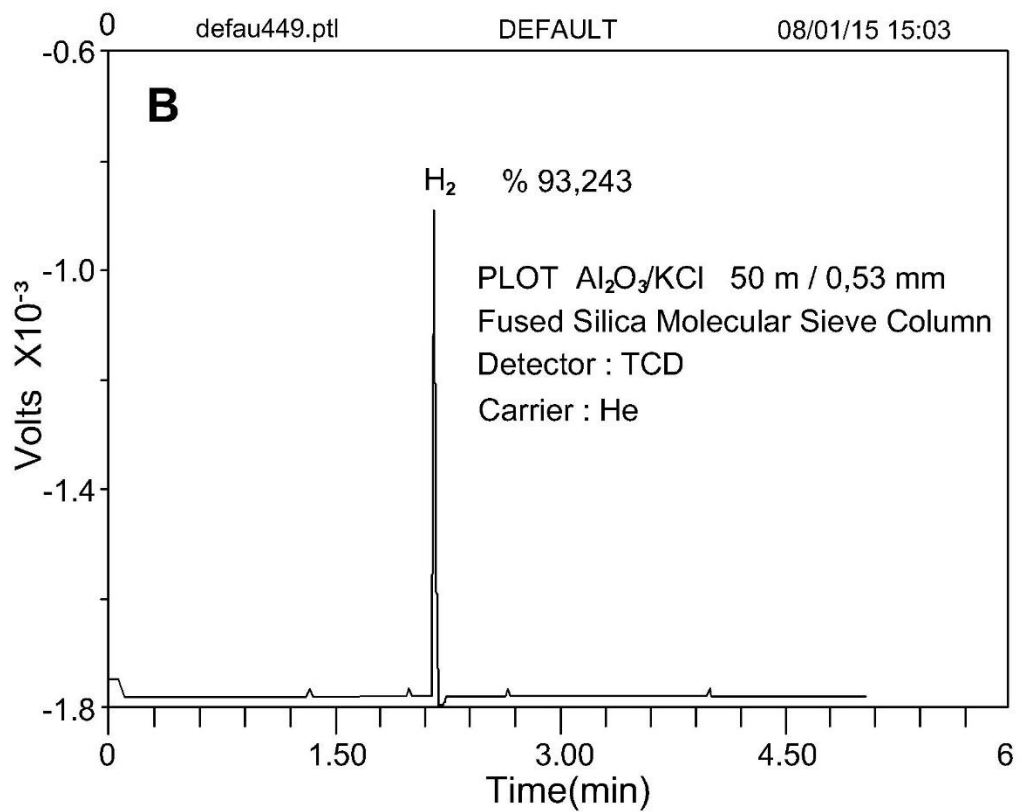
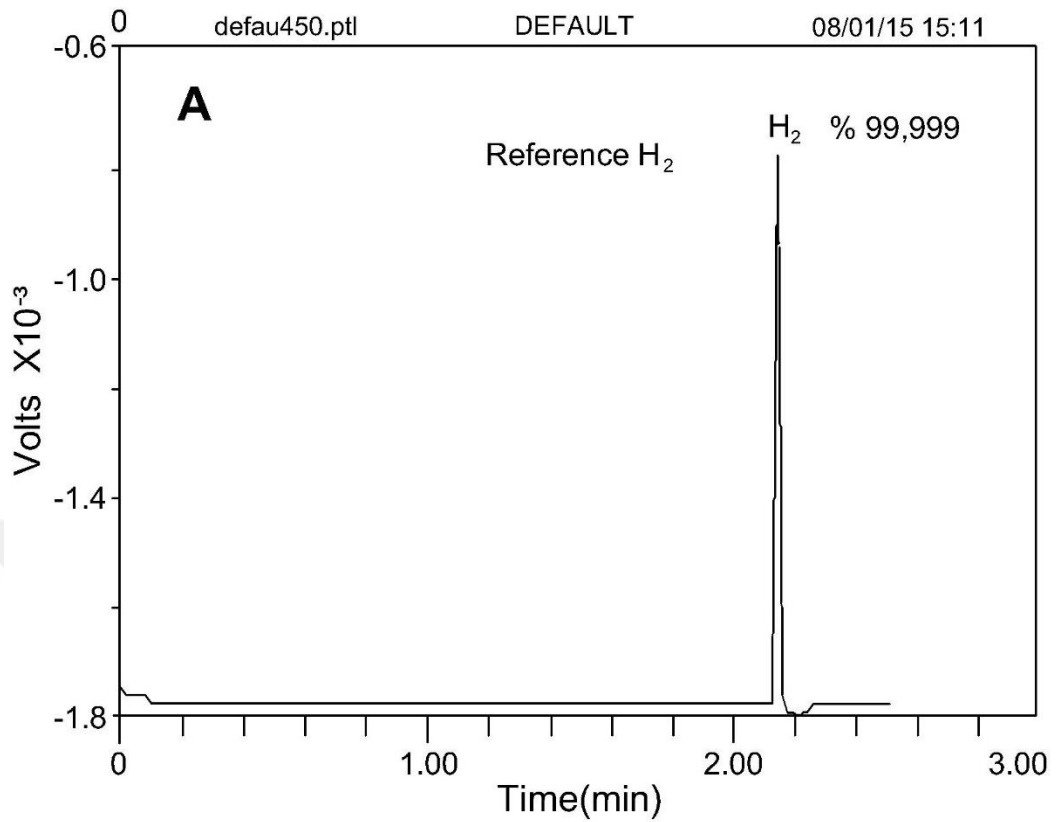


Figure 4.4 Gas Chromatography (GC) spectrum of (A) pure hydrogen gas and; (B) the gas mixture obtained from the reaction of Al dross with water

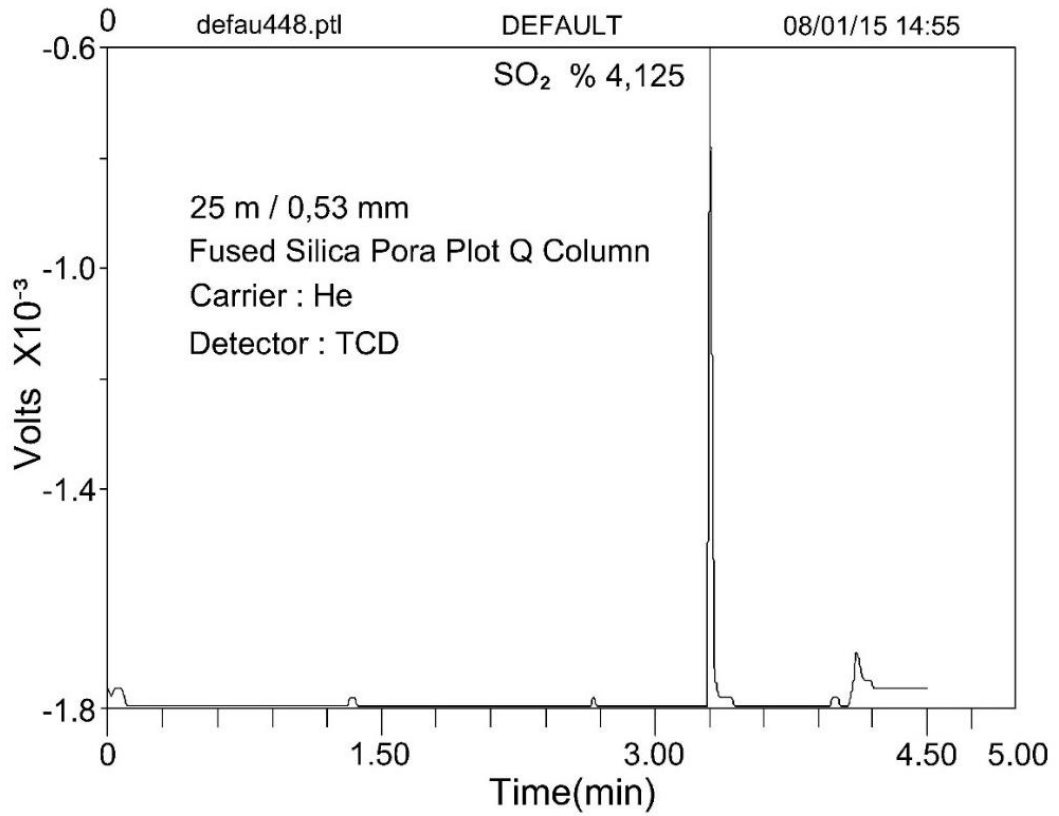


Figure 4.5 Gas Chromatography (GC) spectrum of SO₂ gas

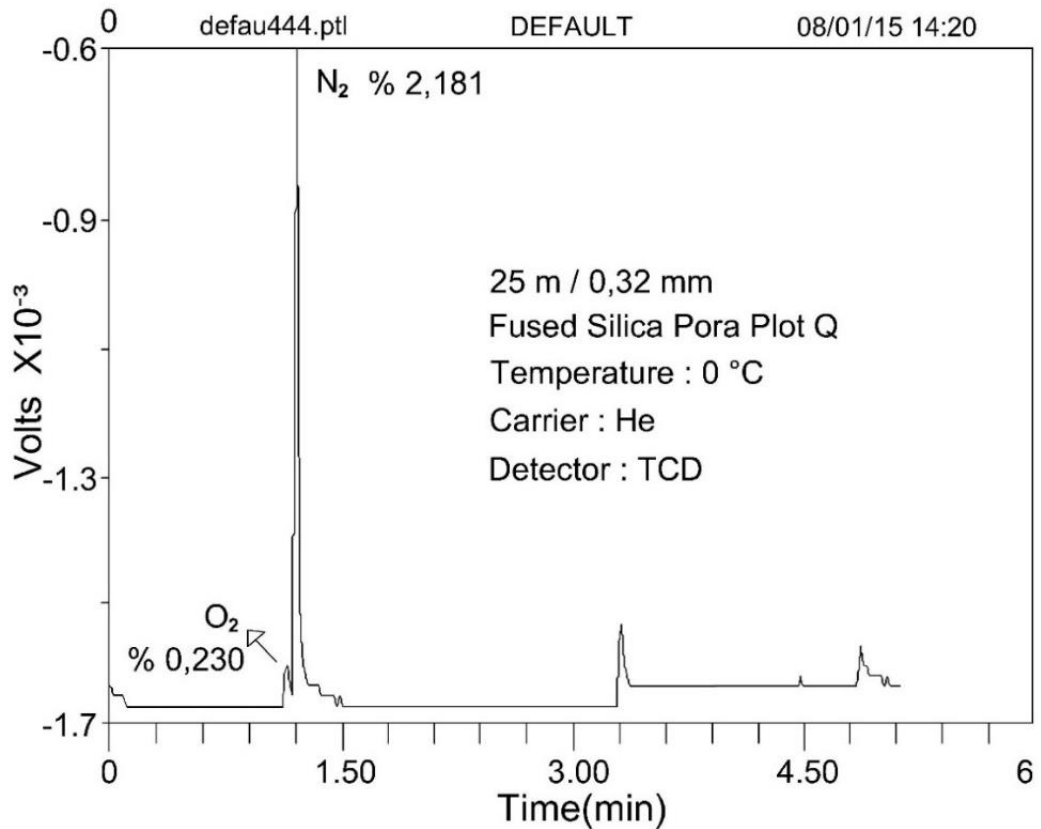


Figure 4.6 Gas Chromatography (GC) spectrum of N₂ and O₂ gas

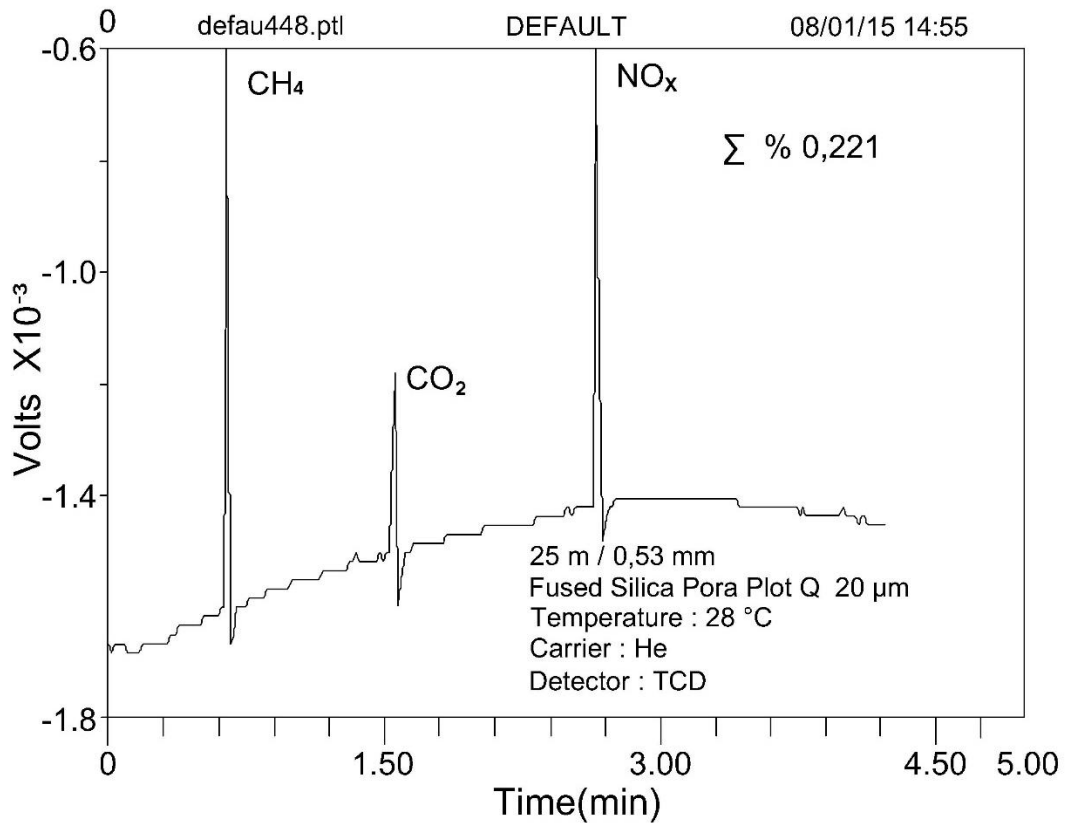


Figure 4.7 Gas Chromatography (GC) spectrum of CO₂, CH₄ and C₁-C₆ hydrocarbons gas

4.6 Calorimeter values

The calorific value of the gas mixture is shown in Table 4.1 and it is very close to calorific value of pure hydrogen gas. The Al dross/water mass ratio, initial water temperatures and system pressure have been determined to be the most significant parameters of the HPR system. In this system, the reaction is exothermic and so heat obtained in larger capacity production facilities can be used for various areas. After reaction is over, the newly formed products, AlO(OH) and Al(OH)₃ will not react with water anymore. The final product becomes harmless and it can be used as a fill material in various fields to manufacture calcium aluminate cement or high quality refractory material [38].

Table 4.1 Comparison of the heating values of pure hydrogen and the gas mixture obtained from the reaction of Al dross with water

Gas	Lower heating value (MJ/m ³)	Lower heating value (MJ/kg)
Pure hydrogen	10,7 [64]	120 [64]
Gas mixture	9,9	110,5

4.7 Discussion

The Al dross+water mass, initial water temperatures and the pressure of the reaction mixture with respect to time have been determined to be the most affecting performance parameters of the HPR system. In this study, a continuous gas outlet becomes due to a chemical reaction in the reactor and it causes the pressure to rise. This reaction is spontaneous and cannot be spent on any form of energy. Because the reaction is exothermic and so more heat can be obtained in larger capacity production facilities. This heat can be used for various application areas. When Al dross+water mixing ratios increased, it is seen that the heat and pressure rises. Based on this study, when large plants are established in the future, we can produce hydrogen gas that results in higher pressures and temperatures without any extra spent energy. It provides energy saving for hydrogen gas storage. In addition, if the hydrogen gas is used in closer places to the manufacturing plant, the transport to the site can be done with installation using its own pressure.

After Al dross-water reaction is over, of the reaction mixture contains new products such as; $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$, which will not react with water again. The final product becomes harmless and it can be used as fill material in various fields and refractory materials. Hence, hydrogen produced by aforementioned method can be seen as a renewable energy production method without any fossil fuel consumption and correspondingly without any environmental pollution.

CHAPTER 5

CONCLUSIONS

The amount of hydrogen (93,243% purity) in the gas mixture and the gas mixture's calorific value (2375 kcal/m³) were determined after collecting the gas mixture which was formed by the reaction of Al dross with water in a specially built reactor.

It was observed that increasing Al dross/water mass ratio, increasing the reaction temperature and increasing the reaction pressure increased the hydrogen generation rate with other variables kept constant.

The induction time has been shortened by increasing temperature and increasing pressure.

Local temperature increases due to the exothermic character of the Al-H₂O reaction. The highest average volume of hydrogen obtained for the reaction of 1 kg of aluminum dross with 2 L hot tap water (T=100°C) was found to be 120 L and this was achieved within 1 hour.

The experimental results revealed that aluminum dross can be economically recycled by a hydrolysis process which can lead to promising systems for hydrogen generation and for obtaining zero hazardous aluminum dross waste.

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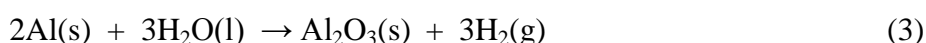
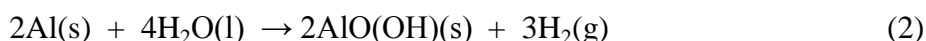
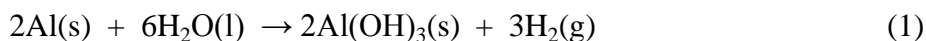
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APPENDIX

Appendix A: Thermodynamics of Aluminum-Water Reactions

The possible reactions of aluminum with water are as follows:



In the first of the possible equations above, the product formed at the end of the reaction is Al(OH)_3 (gibbsite). In the second equation, the product formed at the end of the reaction is AlO(OH) (boehmite) and the product formed at the end of the third equation is Al_2O_3 (alumina). As seen in the Eqs. (1, 2 and 3), the hydration levels of these products are formed at the end of the reaction is different. In all three equations, the same amount of hydrogen according to the amount of aluminum reacted is produced, but the amount of water required for each three reactions is different. All of these reactions thermodynamically occur at a wide temperature range, from room temperature to the melting point of aluminum (660°C). Besides, they are extremely exothermic.

The thermodynamic data according to the temperature of Al(OH)_3 , AlO(OH) and Al_2O_3 reactions using the HSC Thermodynamic Software Program (Version 6.1) are shown in Tables 1-A, 1-B and 1-C. The data in the tables are as shown per mol H_2 .

Table 1-A: Thermodynamic parameters for the aluminum-water reaction in gibbsite formation.

$$2/3\text{Al(s)} + 2\text{H}_2\text{O(l)} = 2/3\text{Al(OH)}_3\text{(s)} + \text{H}_2\text{(g)}$$

T, °C	⊗H, kJ/mol H ₂	⊗S, J/K	⊗G, kJ/mol H ₂
0	-277	26.2	-284
100	-284	3.29	-286
200	-291	-12.1	-285
300	-298	-25.1	-283
400	-306	-38.0	-280
500	-316	-51.8	-276
600	-328	-66.8	-270
700	-350	-90.9	-262
800	-369	-109	-252
900	-391	-128	-240
1000	-417	-149	-232

Table 1-B: Thermodynamic parameters for the aluminum-water reaction in boehmite formation.

$$2/3\text{Al(s)} + 4/3\text{H}_2\text{O(l)} = 2/3\text{AlO(OH)(s)} + \text{H}_2\text{(g)}$$

T, °C	⊗H, kJ/mol H ₂	⊗S, J/K	⊗G, kJ/mol H ₂
0	-267	83.3	-289
100	-279	39	-294
200	-285	26.6	-297
300	-291	13.8	-299
400	-302	-2.69	-300
500	-312	-17.4	-299
600	-323	-30.5	-296
700	-341	-49.9	-292
800	-352	-60.3	-287
900	-362	-69.8	-280
1000	-373	-78.5	-273

Table 1-C: Thermodynamic parameters for the aluminum-water reaction in alumina formation.

$2/3\text{Al(s)} + \text{H}_2\text{O(l)} = 2/3\text{Al}_2\text{O}_3\text{(s)} + \text{H}_2\text{(g)}$			
T, °C	⊗H, kJ/mol H ₂	⊗S, J/K	⊗G, kJ/mol H ₂
0	-272	62.1	-289
100	-275	51.1	-294
200	-279	43.1	-299
300	-283	35.5	-303
400	-288	27.3	-306
500	-294	18.1	-308
600	-303	7.80	-310
700	-320	-11.3	-309
800	-333	-23.7	-308
900	-348	-37.1	-305
1000	-366	-51.6	-304

In all of these equations, the enthalpy value is extremely exothermic. The average of three reactions are -279 kJ/mol H₂ at 100°C and -337 kJ/mol H₂ at 700°C. In addition, we can see that Al₂O₃ becomes more thermodynamic and more positive than Al(OH)₃ and AlO(OH) at higher temperatures.

As it can be seen, Al(OH)₃ is the most stable component from room temperature to 280°C, and AlO(OH) is the most stable component from 280°C to 480°C. Above 480°C, Al₂O₃ is the most stable compound. This means that at room temperature the reaction product of aluminum with water will be aluminum hydroxide Al(OH)₃ [21].

In Figure 1-A in (3) below, the free energy of aluminum hydroxides as compared to aluminum oxide is shown:

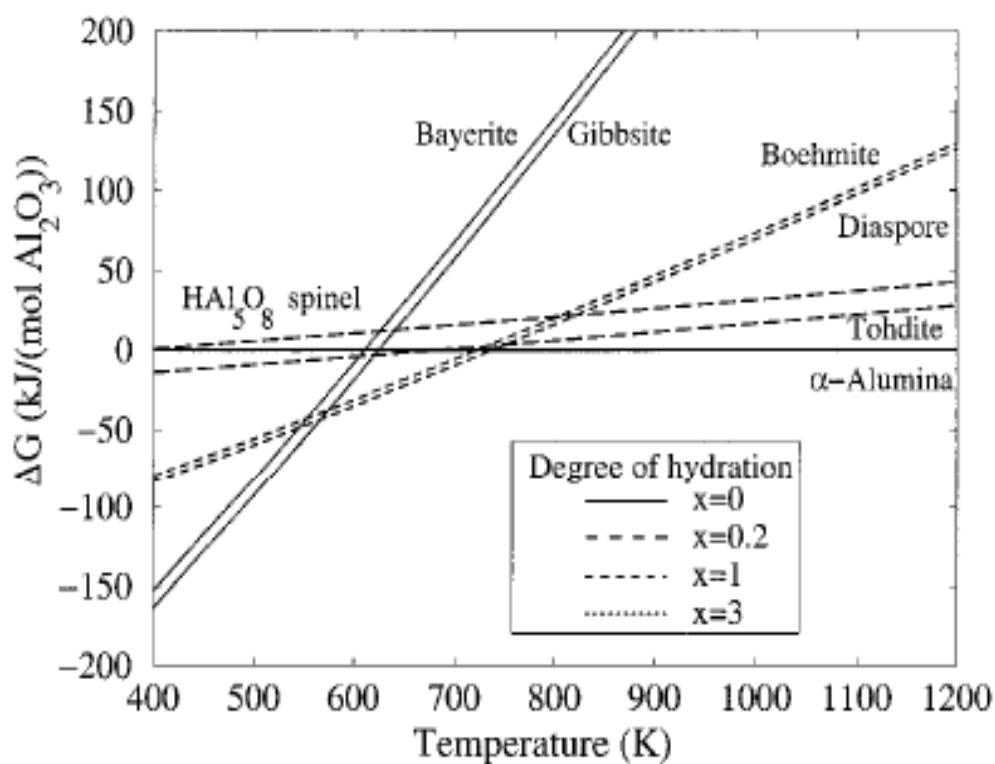


Figure 6. Gibbs free energy of the aluminum hydroxides compared to α - Al_2O_3 (see eq 3), as a function of temperature and for different aluminum hydroxides. The energy is expressed per Al_2O_3 formula unit.

TABLE 8: Thermodynamical Stability of Aluminum Hydroxides (See Text for Definitions)

compound	unit cell $y[\text{Al}_2\text{O}_3, x\text{H}_2\text{O}]$	$\Delta G(298 \text{ K})$ (kJ/(mol Al_2O_3))	T_{inv} (K)	T_{exp}^a (K)
α -alumina	$2[\text{Al}_2\text{O}_3, 0\text{H}_2\text{O}]$	0		
tohdite	$5[\text{Al}_2\text{O}_3, 0.2\text{H}_2\text{O}]$	-17.7	698	> 900
boehmite	$2[\text{Al}_2\text{O}_3, \text{H}_2\text{O}]$	-97.5	719	> 720
diaspore	$2[\text{Al}_2\text{O}_3, \text{H}_2\text{O}]$	-101.4	731	770
bayerite	$8[\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}]$	-206.8	609	> 500
gibbsite	$8[\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}]$	-217.5	624	> 570

Figure 1-A Thermodynamic stability of aluminum hydroxides according to temperature (Figure 6 and Table 8 in Reference 4)

Appendix B: Examples of some organizations that produce hydrogen production by aluminum-water reactions [21]

Organization	Product	Website
Hydrogen Power Inc.	AlumiFuel Cartridge	http://www.hydrogenpowerinc.com
Altek Fuel Group Inc.	Hydrogen Fuel Cartridge	http://www.altekfuel.com
Purdue University	Aluminum-Gallium Alloys	http://hydrogen.ecn.purdue.edu/
HydPo Ltd.	Hydrogen from aluminum-water reaction	No website available Email contact: yossi@hydpo.com

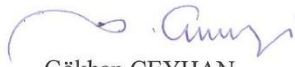
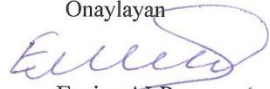
Appendix C: XRF analysis results performed in ÜSKİM laboratory

	KAHRAMANMARAŞ SÜTÇÜ İMAM ÜNİVERSİTESİ ÜNİVERSİTE-SANAYİ-KAMU İŞBİRLİĞİ GELİŞTİRME, UYGULAMA VE ARAŞTIRMA MERKEZİ (ÜSKİM) LABORATUVARI AVŞAR KAMPÜSÜ / KAHRAMANMARAŞ		DG-XRF.04707
	Tel:(0344) 280 18 80 / FAX: (0344) 280 18 81		
	uskim@ksu.edu.tr	uskim.ksu.edu.tr	01.15
	Deney Raporu <i>Test Report</i>		
Müşterinin Adı /Adresi <i>Customer Name /Adress</i>	:	Mehmet KALE / Gaziantep Üniversitesi Makine Mühendisliği Bölümü	
İstek Numarası <i>Order No.</i>	:	DG-XRF.04707	
Numunenin Adı ve Tarifi <i>Name and identity of test item</i>	:	Atık Alüminyum	
Numunenin Kabul Tarihi <i>The date of receipt of test item</i>	:	27.01.2015	
Açıklamalar(Numune Koruma İşlemleri vb.) <i>Explanations</i>	:	1 Nolu numune	
Deneyin Yapıldığı Tarih <i>Date of test</i>	:	27.01.2015	
Raporun Sayfa Sayısı <i>Number of pages of the Report</i>	:	2	
<p>Türk Akreditasyon Kurumu(TÜRKAK) deney raporlarının tanınması konusunda Avrupa Akreditasyon Birliği(EA) ve Uluslararası Laboratuvar Akreditasyon Birliği(ILAC) ile karşılıklı tanınma antlaşmasını imzalamıştır.</p> <p><i>The Turkish Accreditation Agency(TURKAK) is signatory to the multilateral agreements of the European co-operation for the Accreditation(EA) and of the International Laboratory Accreditation(ILAC) for the Mutual recognition of test reports.</i></p> <p>Deney ve /veya ölçüm sonuçları, genişletilmiş ölçüm belirsizlikleri (olması halinde) ve deney metotları bu sertifikanın tamamlayıcı kısmı olan takip eden sayfalarda verilmiştir.</p> <p><i>The test and/or measurement results, the uncertainties (if applicable) with confidence probability and test methods are given on the following pages which are part of this report.</i></p>			
	Tarih <i>Date</i>	Laboratuvar Sorumlusu <i>Person in Charge of Laboratory</i>	Merkez Laboratuvar Koordinatörü <i>Head of Testing Laboratory</i>
	28.01.2015	 Gökhan CEYHAN Uzman Dr.	 Evrim ALP Kimya Yüksek Mühendisi

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Sayfa 2 / 2 Page	KAHRAMANMARAŞ SÜTÇÜ İMAM ÜNİVERSİTESİ ÜNİVERSİTE-SANAYİ-KAMU İŞBİRLİĞİ GELİŞTİRME, UYGULAMA VE ARAŞTIRMA MERKEZİ (ÜSKİM) LABORATUVARI AVŞAR KAMPÜSÜ / KAHRAMANMARAŞ TEL: (0344) 280 18 80 FAX: (0344) 280 18 81 uskim@ksu.edu.tr uskim.ksu.edu.tr		DG-XRF.04707 01.15
	Numuneyi Gönderen :	Mehmet KALE	Numune Kabul Tarihi :
Ait Olduğu Proje :	-	Deney Başlama Tarihi :	27.01.2015
Numune Tarifi :	Atık Aliminyum	Deney Bitiş Tarihi :	27.01.2015

XRF Analiz Sonuçları	
Formula	Concentration
Al	41,96%
Ca	18,30%
Cl	8,02%
Si	6,24%
Mg	6,16%
Ti	4,92%
Ba	3,29%
Fe	2,72%
S	2,51%
Na	1,92%
K	1,76%
Zn	0,64%
P	0,48%
Cu	0,30%
Pb	0,25%
Mn	0,13%
Ni	0,13%
Sr	0,11%
Cr	0,10%
V	0,04%
Br	0,01%
Mo	0,01%
Ga	99 PPM
Co	31 PPM

Laboratuvar Sorumlusu  Gökhan CEYHAN Uzman Dr.	Onaylayan  Evrım ALP Kimya Yüksek Mühendisi
Notlar: 1) Deneyler, talep sahibi tarafından laboratuvarımıza teslim edilen deney numuneleri üzerinde gerçekleştirilmiştir. 2) (*) işaretli olan deney/deneyler, akredite olunan deneyi/deneyleri göstermektedir. Ölçüm belirsizliği, deney süresindeki belirsizlikleri kapsamaktadır ve % 95 (k=2) güven aralığında hesaplanmıştır. 3) Bu rapor, İstek No DG-XRF.04707 sayılı ön yazı ile bir bütündür. 4) Deney tekrar istenmesi halinde laboratuvarımızda numune kalmamıştır. <input type="checkbox"/> / Şahit numune süre sonunda imha edilecektir. <input type="checkbox"/>	
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Appendix D: The analysis parameters of gas mixtures

SENTEZ
MÜHENDİSLİK MÜŞAVİRLİK ARITMA SAN. ve TİC. LTD. ŞTİ.



ANALİZ RAPORU

FİRMA ADI : LİDER MÜHENDİSLİK
FİRMA ADRESİ : 23 Nisa Mah.Üniversite Bulvarı.Başel Apart.No:269/C
Şahinbey/GAZİANTEP
FİRMA REFERANS NO : -
ÜRETİCİ FİRMA : -
ÖRNEK CİNSİ : Hidrojen Gazı
ÖRNEĞİN ALINDIĞI YER : -
AMBALAJ CİNSİ : Çelik Tüp
MİKTAR : 2 adet
ÜRETİM TARİHİ : -
SON KULLANMA TARİHİ : -
SERİ NO : -
GELİŞ TARİHİ/SAATİ : 14.01.2015 / 11:30
ANALİZ TARİHİ : 14.01.2015/120.01.2015
RAPOR TARİHİ : 20.01.2015
RAPOR NO : R0150015
SAYFA NO : 1

14.01.2015 tarihinde laboratuvarımıza göndermiş olduğunuz " Hidrojen " gazı örneğinde talep edilen analizler "ASTM" göre yapılmış olup, sonucu aşağıda bilgilerinize sunulmaktadır.
Tüm ölçümlerimiz, TSE ve İngiliz (Aqua Check)'den akredite laboratuvarımızda APHA, EPA, ASTM, UMA, ISO, EN, TSE gibi ulusal ve uluslar arası otoriteler tarafından kabul edilmiş standart metodlara tam uyumlu olarak, literatürde belirtilen kalite ve hassasiyetteki cihaz, malzeme ve ekipmanlar ile yapılmaktadır.
Laboratuvarımız TSE tarafından TS EN ISO/IEC 17025'e göre denetlenmektedir.

<u>Analiz parametreleri</u>	<u>Bulgular</u>
Hidrojen	%93.243
Azot	%2.181
Oksijen	%0.230
Kükürt dioksit	%4.125
Geri Kalan(CO ₂ ,CH ₄ ,C ₁ -C ₆ Hidrokarbonlar)	%0.221
Kalorifik Değer	2,375 kcal/m ³

Saygılarımızla,
Dr. Reha DURO
Kimya Yük.Müh.
Genel Müdür

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Bu raporda bildirilen sonuçlar yukarıda açıklanan örnek içindir.

FR.060/11.07.2014-02

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