Comparative study of Hydrogen yield from magnesium waste products in Acetic acid and Iron chloride solution

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Low-grade magnesium (Mg) waste from post-consumer products and production waste cannot be recycled efficiently and economically. This work addresses this challenge by converting this waste into hydrogen. Hydrogen (H2) offers a wide range of benefits and the greatest of them all is its ability and flexibility to be used as a green energy carrier. In this work Mg waste is re-melted, loaded on one side of a stainless steel and allowed to solidify at room temperature to form a galvanic Mg stainless steel couple. Mg reacts slowly with water and releases hydrogen at room temperature and this is followed by the formation of magnesium hydroxide on its surface. Stainless steel net is considered as a metallic catalyst and two acids as accelerators reacting with the couples separately. A set of couples were used to generate hydrogen in 3.5% by weight acetic acid (CH_3COOH). The experimental results show that a mean accumulated H_2 volume of 3.17 – 3.21 litres was produced in 3600 seconds. Another set of couples produced H2 in 1.5 wt. % of iron chloride ($FeCl_3$). The results confirmed $FeCl_3$ as an excellent hydrolysis reaction accelerator with stainless steel as an effective catalyst. On average, the reaction yielded 2700mL of H2 over 3600 seconds which appear to be substantially higher than the litres achieve when CH_3COOH was considered as an accelerator.

Keywords-hydrogen; waste magnesium; hydrolysis reaction; acetic acid; iron cloride

I. INTRODUCTION *(HEADING 1)*

Energy is one of the fundamentals in the modern life, it is needed for everyday activities. The major energy resources include, coal, petroleum and natural gases. Burning these, carbon-based fuels generate carbon dioxide and others, which can cause environmental air pollution, which cause global warming [1]. Global warming can increase the average temperature in the entire world gradually. Hydrogen South Africa (HySA) is one of the three National Competence Centres which was initiated by Department of Science and Technology and was approved in May 2007, as a long term program within the hydrogen research. The programme aimed at developing South African participation in hydrogen and fuel cell technologies [1]. Global warming result in climate change. Finding renewable energy resources is one of the urgent issues in the world. Hence hydrogen is considered, as a safe, clean, environmental friendly, and has high efficiency and good stability.

Hydrogen generation is already being widely used in applications such as transportation and power generation. Hydrogen is a source of energy with a lot of potential due to its renewable nature [2]. One of the major challenges of hydrogen energy is storage. In various studies, which have been conducted recently, metal hybrids are considered as one of the hydrogen storage media. One of the densest storage of hydrogen which has about 10.6% of hydrogen by weight is lithium aluminium hydride ($LiAlH_4$).

There are other types of hydrogen storages which are considered like solid hydrogen storage, high pressure hydrogen storage, chemical bond hydrogen storage, solid hydrogen storage and liquid hydrogen storage. One of the safest hydrogen storage methods are sodium borohydride ($NaBH_4$), this method is also famous for generating high quality hydrogen gas without polluting emissions. The major problem with this method is that the production cost of sodium borohydride is too high [3]. Presently hydrogen is mostly used as a chemical rather than as a fuel. Hydrogen can be used as an alternative source of energy to fossil fuels, hydrogen can be produced from fossil fuels. Fossil fuels are the mostly used type of energy in South Africa and in the entire world. Fossil fuels can cause pollution and global warming. Because of its higher efficiency, electrolysis is the most dominant technology used for hydrogen production from renewable sources.

South Africa is one of the countries that are accounted to have large coal reserves and platinum group metals (PGM). South Africa accounts for approximately 80% of the world's annual platinum production and an estimated 88% of the world's platinum reserves. And most of these platinum group metals can be used to produce hydrogen. And the current energy is produced from coal, which is fossil fuels. 75% of South Africa's primary energy is supplied by coals. Because South Africa have large CO_2, then it is ranked twelfth highest in the world (2012) [4]. Energy is a lifeline of any economy. Because of those resources South Africa can implement hydrogen and in addition it will benefit in several ways; the economic growth will increase and, South Africa will also contribute significantly to the solution of global climatic challenge. The platinum group metals can be used to produce hydrogen.

The South African energy supply is dominated by coal with 59% of the primary energy supply followed by renewables with 20% and crude oil with 16%. Natural gas contributed 3% while nuclear contributed 2% to the total primary supply in 2015. The primary energy supply in this case includes indigenous energy production and imported energy sources. Figure 1 below shows South Africa's energy consumption for the year 2015.

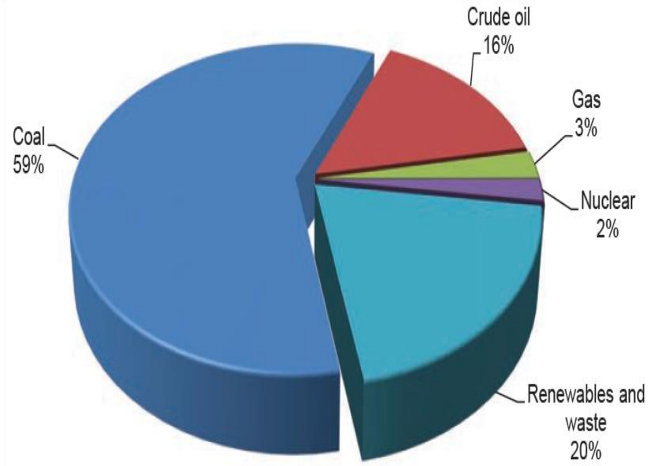

Fig. 1 South Africa's energy consumption for the year 2015 [1]

Sources of Magnesium Scrap

Scrap metals can be divided into two broad categories such as production and obsolete scrap. Production scrap is the scrap resulted from waste metals generated during the manufacturing and production of metal products. Production scrap is easily identified in the form of turning or shavings, off-cuts, trimmings and stampings. In the foundries, mini-mills and mills this scrap is generated melting processes and this is usually reused or recycled in-house, without being sold to the recyclers [4].

The obsolete scrap is the metal products that have reached the end of their life span. This includes a wide range of metal products and products containing metal. Material from the automotive, electronics, telecommunications, audio and computer industries. Because of the recent increase in the use of magnesium in the vast automotive market, the amount of post-consumer magnesium scrap is growing rapidly[5, 6].

Magnesium (Mg) is 33% lighter than aluminum, 100% recyclable, and has one of the highest strength-to-weight ratios of any of the commonly used metals, it has been chosen as a substitute for many automotive components [5]. Mg can be described as a silver-white, grey alkaline earth metal with an atomic number 12, and is the 8th abundant element in the world, and it is capable of producing highly flammable gases when reacted with water [4]. Magnesium alloys are one of the slightest, and are mostly used in the automotive industries for parts manufacturing. The environment requires light-mass materials for transport to reduce harmful emissions. Magnesium alloys are corrosion resistance, and therefore require coating. Although magnesium is a recyclable material, only one third of magnesium scrap are recycled, there rest is buried or burned [12]. An interesting possibility is to employ such a waste for producing materials for H_2 storage [7]. For the development of fuel cells, compact, safe and inexpensive H_2 source is a key issue. Research work is on-going to investigate different sources of H_2. These include compressed H_2, carbon-based H_2 storage, metal hydrides, chemical hydrides and methanol. [6, 8]. Chemical hydrides can be handled in a semi-liquid form, such as mineral oil slurry [8].

Enhancing Hydrogen Generation

The use of catalysts in H_2 generation is reported in literature where it is claimed that catalysts improved the reaction kinetics. These catalysts include organic acids, strong acids and earth metals. Organic acids such as acetic acid have been reported to improve H_2 generation rate [9, 10]. Organic acids are preferred due to their friendliness to the environment, low cost and availability [10]. On the other side, strong acids such as hydrochloric acid, sulphuric acid and phosphoric acid have also been reported to improve the reaction kinetics [9, 10]. Adkin [10] concluded that acetic acid which is a weak acid has almost the same effect on results for H_2 generation potential. Stainless steel, titanium and platinum have been reported as catalysts in H_2 generation experiments to improve the thermodynamic properties of the reaction and the results are outstanding [11, 12].

For this study, an inorganic acid known as iron chloride ($FeCl_3$) also known as ferric chloride is explored and considered as an accelerator. It is an industrial chemical compound which appears dark green upon light reflection and purple-red by transmitted light. It dissolves in water [13] and undergoes hydrolysis where heat is generated in an exothermal reaction. The results of the exothermal reaction are a brown acidic and corrosive solution that is reported to be used extensively in drinking water purification plants, as a flocculent in sewage treatment plants and in the production of printed circuit boards. According to [14] $FeCl_3$ is extensively used in organic synthesis as an ideal Lewis acid since it is an inexpensive, efficient, stable, environmentally friendly and a convenient agent for several useful reactions.

Magnessium Production

Mg is reportedly produced in China, Russia, Turkey, Austria, Slovakia, North Korea, Brazil, Spain, Greece, India and Australia in thousands of tonnes. Mg is produced from seawater (1.3 kg m^{-3}), well and lake brines, and bitterns, as well as from ore magnesite ($MgCO_3$), dolomite ($MgCO_3CaCO_3$), and magnesite. It is 30% lighter than aluminium and the lightest structural metal used today as an alloy [15, 16]. Mg is reported to be the third most used metal after iron and aluminium in the construction industry. About 70% of Mg produced worldwide is used to produce low density alloys which ultimately have comparative high strength and excellent machinability. Mg alloys are widely used in the automotive and aircraft sectors. Only 3% of the total annual production is recycled.

Post-consumer Magnessium Scrap

A large amount of Mg scrap comes from the automotive industry followed by electronics, telecommunications, audio and computer industries [5]. Recent reports indicate a significant increase in the use of Mg based components in the automotive industry and this has increased the amount of scrap that is being collected from this industry. When a vehicle has reached its end-of-life and sent for scrap collection, 50% of the weight of the original vehicle is dismantled in the dismantling yard. The remaining portion is pressed in the presses for volume reduction. The pressed volume is then sold to the shredder plants [5] where several shorting processes take place to separate the materials according to classes. The known challenges with sorting Mg scrap include the very high cost of equipment and contamination during the sorting process [2, 12]. This study also seeks to further contribute towards promoting the recycling of the end-of-life Mg products for use in H_2 generation.

Magnessium Based Materials in Hydrogen Generation - an Overview

Uan et al. [2] studied a mixture of low-grade Mg scraps and citric acid-added seawater to generate H_2 gas. In this study, metal catalyst was not used as it was not required for accelerating the reaction of H_2 generation in the Mg scraps and citric acid solution. The results indicated that 20 wt. % citric acid added seawater can produce substantially higher H_2 volume than 5 wt. % citric acid-added seawater. After dehumidification the H_2 purity was about 99%. This was achieved by filling the H_2 production reactor every 30 minutes with fresh seawater to citric acid and w70 litre of H_2 could be produced in 100 minutes.

Grosjean et al. [17] investigated H_2 production by hydrolysis of Mg-based materials particularized by high-energy ball milling. MgH_2 (95 wt. % MgH_2, 5 wt. % Mg, 20μm), Mg and Ni (99.8 wt. %, −325 mesh) were considered in this investigation and the best results were obtained with Mg–10at. %. Ni composite material milled for 30 min, which leads to a conversion yield of 100% after 1 h of hydrolysis in neutral aqueous solution containing chloride ions.

Huang et al. [18] investigated the use of waste Mg based material as a raw material for the generation of H_2. Ball milling and saline solution method were performed to ensure full completion of the hydrolysis reaction. Saline solutions that were tried include $NiCl_2$, $CoCl_2$, $CuCl_2$, $FeCl_3$, and $MnCl_2$. The results show a maximum conversion of 100% was achieved in $NiCl_2$ solution.

Uan et al. [11] studied generation of H_2 from Mg alloy scraps catalysed by platinum-coated titanium net in NaCl aqueous solution. The H_2 generation rate was found to be around 302.3ml per minute (g of catalyst weight per minute) for 1600 seconds when the net was placed statically on top of the sample. When the net was inserted inside the sample Mg, the rate of H_2 production improved significantly by around 7.5 times compared to generated H_2 when the catalyst was statically loaded on the surface of the Mg sample.

Uan et al. [12] investigated H_2 production where a platinum-coated titanium net and 304 stainless steel net were used as metallic catalysts. The mean volume of H_2 generated in 50 minutes was 5.7 litres when the catalyst was platinum-coated titanium and 7.8 litres when stainless steel was used as a catalyst.

II. EXPERIMENTAL

In the present study, the corrosion reaction of the hydrogen generating reaction containing 3.5% CH_3COOH by weight in water solution and 1.5% $FeCl_3$ by weight added water solution is studied. The 3.5% CH_3COOH was prepared by dissolving 19.95 litres of CH_3COOH in 550.05 litres of normal tap water. The 1.5 wt. % $FeCl_3$ was prepared by dissolving 8.6 ml of $FeCl_3$ in 561.42 ml of normal tap water. Mg-stainless steel net couples were placed inside a 500 ml glass reactor vessel and $FeCl_3$ added water solution injected. The procedure was followed when the solution included CH_3COOH.

Low grade Mg waste is used to produce H_2. Low-grade Mg couples are prepared from melted Mg end-of-life products, allowed to solidify onto a stainless steel net as depicted in Fig.2. This is performed to effectively study and evaluate the ability of the metal catalytic net on improving H_2 yield. The chemical composition of the re-melted Mg scrap is between 65 – 80.2 wt. % Mg, 2.3 – 7 wt. % Al, 9 – 12.2 wt. % O_2 and a few other traces of elements as shown in Fig 3 and 4.

Fig. 2 Stainless steel net over layered with molten and solidified low grade Mg on one side on the net

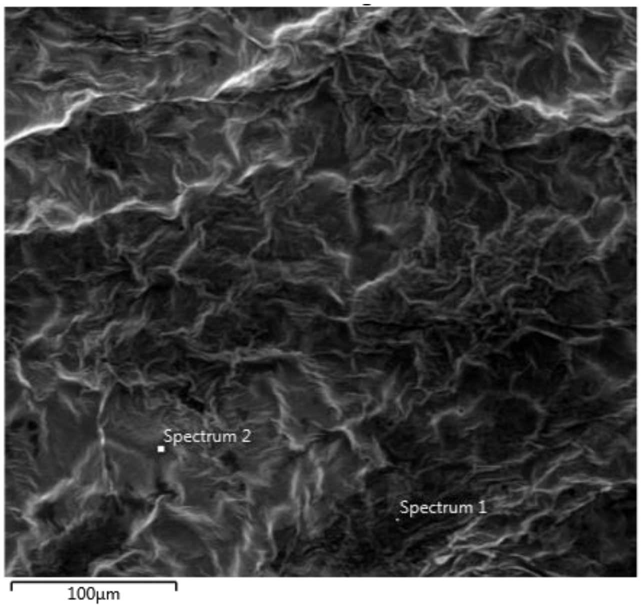

Fig. 3 Spectrum analysis

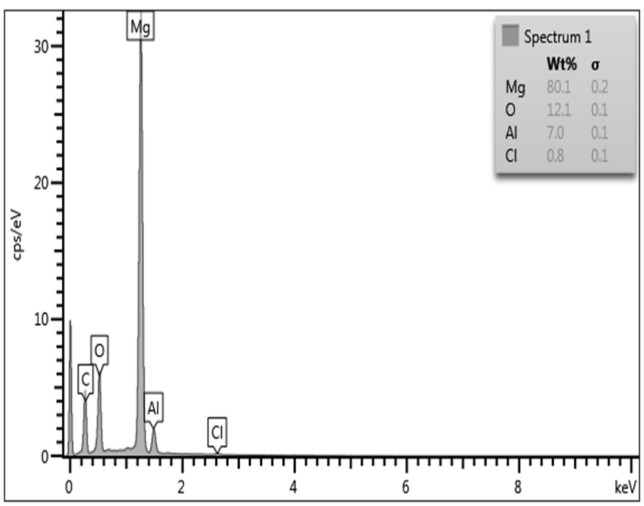

Fig. 4 Material analysis

Fig. 5 depicts the experimental set-up used in this study. Mg sample is placed inside the reactor, prepared solution is injected through the burette ensuring that no air enters the system. A humidifier is considered to ensure that any vapour is effectively removed and only dry gas can be measure from the flow meter. The data from the flow meter is collected and stored in a personal computer for analysis.

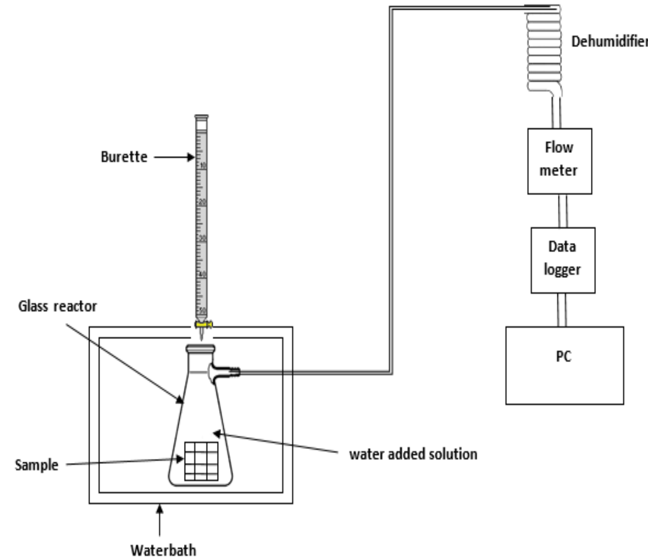

Fig. 5 Experimental set-up schematic diagram

III. RESULTS

The corrosion for Mg waste in water generates hydrogen and Mg hydroxide[9, 19]. To promote significant rate of H_2 generation, this reaction is catalysed by stainless steel net. Hence, the chemical reactions in this study are expressed as follows:

$$Mg + 2H_2O \xrightarrow[\text{Catalyst}]{\text{CH3COOH Solution}} H_2 + Mg\,(OH)_2 \qquad (1)$$

$$Mg + 2H_2O \xrightarrow[\text{Catalyst}]{FeCl_3\ \text{Solution}} H_2 + Mg\,(OH)_2 \qquad (2)$$

Fig.6 and 7 plots the H_2 generation rate when $FeCl_3$ and CH_3COOH are used as accelerators against time, respectively. The study notes the significant generation rate in the first 2 minutes for both cases. The generation rate for $FeCl_3$ increases to about 1.6 litres per minute in the first 0-2 minutes which is significantly higher that what is achieve when CH_3COOH is used. Thereafter, the generation rate decreases over time.

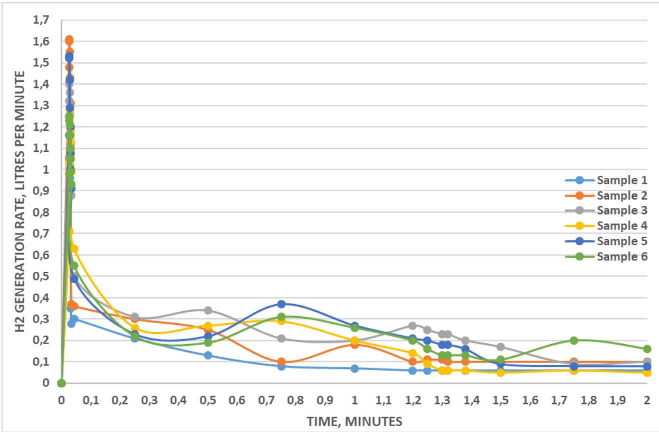

Fig. 6 H_2 generation rate for the first 2 minutes when $FeCl_3$ is used as an accelerator

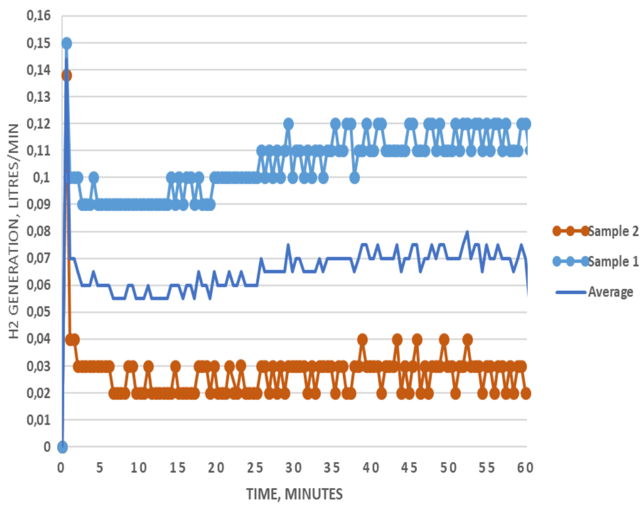

Fig. 7 H_2 generation rate for the first 60 minutes when CH_3COOH is used as an accelerator

Fig.8 and 9 plots the cumulative H_2 volume from the start of the reaction up to 60 minutes. It can be noted from the figures that the cumulative H_2 volume increase with time.

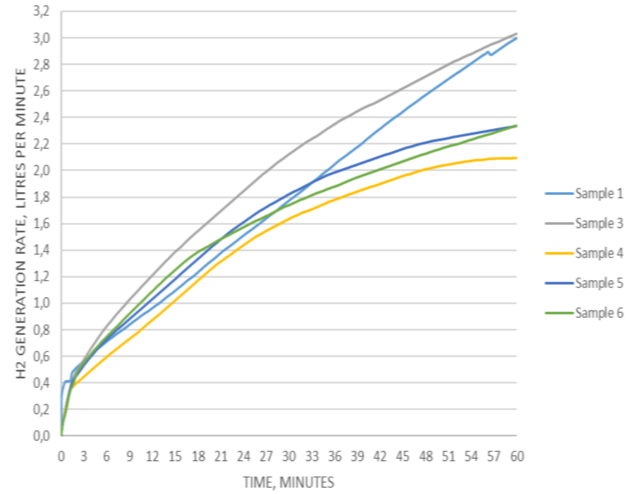

Fig. 8 Cumulative H_2 volume after 60 minutes when $FeCl_3$ is used as an accelerator

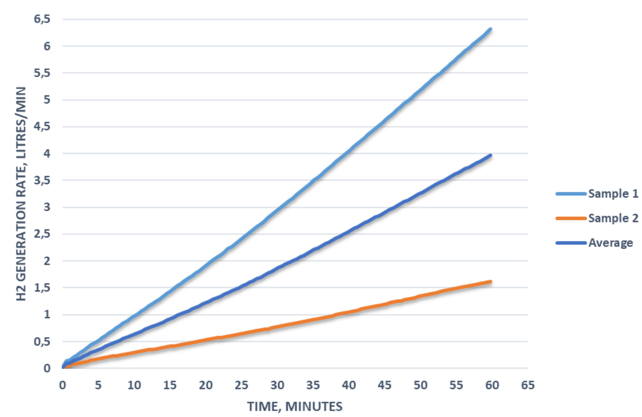

Fig. 9 Cumulative H_2 volume after 60 minutes when CH_3COOH is used as an accelerator

IV. CONCLUSION

This work studied hydrogen generation reaction where Mg waste is used as raw material in 1.5 wt. % $FeCl_3$ added water catalyzed by stainless steel net. $FeCl_3$ also known as iron chloride has proven itself as an effective hydrolysis reaction accelerator due to its corrosive nature. The results are compared to those obtained when 3.5% of CH_3COOH added water solution reacts with Mg waste catalyzed by stainless steel net. The low-grade Mg stainless steel net couples reacted with Acetic acid and generated hydrogen, owing to the galvanic reaction Mg (anode) and stainless steel (cathode) [9]. The results from this work suggest that H_2 generation volume can be increased by increasing the weight/surface area of Mg. A smaller wt. % of $FeCl_3$ was used compared to 3.5 wt. % of CH_3COOH with the assumption that $FeCl_3$ will yield greater volumes due to its corrosive nature. This was confirmed by the results obtained in this study. The future works will focus on larger scale of this work for the powering of fuel cell with the produced gas.

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