

**HYDROGEN GENERATION BY REACTION OF BALL-MILLED MAGNESIUM
POWDER WITH HOT WATER**

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By

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ABSTRACT

Hydrogen is a very promising source of fuel; it has already constituted a significant part of modern innovations for power generation in automobile and space shuttle. Hydrogen can be produced from several sources and as a byproduct of some chemical processes, including the association of magnesium with water. The production yield of this later production method is limited by influences associated with the formation of passive oxide/hydroxide films on the surface of magnesium metal during reaction. The experiments within this project highlight optimization conditions towards improved hydrogen yield via magnesium hydrolysis. Reduced rate of hydroxide layer formation on Mg surface, hence increased production yield, is accomplished by exposing a greater surface area of Mg in contact with water. This has been achieved via ball milling process; Mg powders with greater higher surface area to volume ratios are ball-milled with certain salts (e.g. NaCl and KCl). The weight percentage (wt.%) of these salt within the mixture influences hydrogen production yield by facilitating the creation of reaction sites. Here, these salts produce cavities within the magnesium/salt powdery matrices, thus creating more assessable surface area for water. The experimental results from this work reveal that ball milling duration and weight percentage of salts affect the final size of Mg particle produced. Thus, the maximum hydrogen yield is achieved by controlling these two parameters and the results are further correlated by the microstructure of the samples under scanning electron microscope (SEM).

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DEDICATION

*I DEDICATE THIS THESIS TO MY PARENTS FOR THEIR UNCONDITIONAL LOVE AND
SUPPORT DURING MY ENTIRE LIFE*

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

BMR	Ball to powder mass ratio
EDS	Energy-dispersive X-ray spectroscopy
MJ	Mega joules
ODS	Oxide dispersion strengthened
RPM	Round per minute
SEM	Scanning electron microscope
SMR	Steam methane reformation
XRD	X-ray diffraction

Symbols

$^{\circ}\text{C}$	Degree Celsius
keV	Kilo-electron volt
h	Hour
μm	micrometer (10^{-6} m)

CHAPTER 1

INTRODUCTION

1.1 THE NEED FOR AN ALTERNATIVE SOURCE OF FUEL

The industrial revolution which started in the late 18th century marked the first stage of utilization of coal as an energy source; it was later deployed for steam engines and other industries in the 19th and 20th century. It was during this period that oil started gaining popularity and finally replaced coal as a source of fuel. Currently, we still depend mainly on oil for our daily energy needs. As efficient as they are, crude oil and coal will eventually be exhausted, and their usage causes pollution which can cause serious environmental problems. The later disadvantage is heavily linked increased carbon-dioxide content within the atmosphere that leads to global warming. Considering these facts, we need to divert our attention towards an energy source which is safe and last for a long time: an alternative fuel. There is a large variety of alternative fuels like hydrogen, biomass, biofuels, biodiesel, compressed natural gas etc.; the most promising alternate fuel is hydrogen.

“Hydrogen is the most abundant element on Earth, but less than 1% is present as molecular hydrogen gas H₂” (Schlapbach and Züttel, 2001). However, hydrogen storage and efficient production are still critical issues preventing its commercial application. The hydrogen generation in the past decade was mainly from water electrolysis (Souza *et al.* 2007) or fossil resources via gas reformation (Dicks, 1996). A number of scientific methods for hydrogen production has been reported from metals (Zidoune *et al.* 2004), metal hydrides (Grosjean *et al.* 2006; Hiraki *et al.* 2012; Tayeh *et al.*, 2014) and alloys. These methods are limited by the formation of passive oxide/hydroxide layers on precursor metal surfaces which consequently stops reactions from completing (Petrovic and Thomas, 2008; Huang *et al.*, 2017). The best way to remove these passive films is by acid pickling (Kushch *et al.* 2011) but this method is also corrosive. Scientists have suggested the use of various methods such as changing solution pH (Hiraki *et al.* 2012), ball milling (Alinejad

and Mahmoodi, 2009; Huang *et al.* 2017; Petrovic and Thomas, 2008; Razavi-Tousi and Szpunar, 2016; Wang *et al.* 2014), the use of catalysts (Uan *et al.* 2007), ultrasonic irradiation (Hiroi *et al.* 2011) and carbon materials (Awad *et al.* 2016). However, the most effective methods for generating hydrogen are ball milling which has been performed on various metals such as Mg and Al and their hydrides and composites for hydrogen generation by hydrolysis.

In this research, pure Mg was ball-milled along with two different process control agents (NaCl and KCl) for various ball milling times and optimized for the best milling time and the weight percentage of the process control agents.

1.1.1 Hydrogen as a clean and sustainable Fuel

For the past five decades, industrialists and research scholars have suggested that the use of hydrogen as an alternative energy source to crude oil can solve prevailing global warming problems because of its zero carbon-footprint. Hydrogen is classified as a safe and clean energy source with a promising future. As early as 1874, Jules Verne in his famous novel “*The Mysterious Island*” stated that: “water will be the coal of the future” (Verne, 1874).

Hydrogen (140 MJ/kg) has a relatively high specific energy content and it is abundant on the earth. However, it is present in its oxide form (H₂O) which provides very little use for it as a fuel. With water being the only by-product of hydrogen combustion, hydrogen gas is proven to be a great source for clean energy. Hydrogen can act as a solar storage medium for a later need, and will potentially play an important role in future development of new energy options.

Hydrogen in its native state is gaseous and there are various forms in which hydrogen can be stored. Hydrogen may be stored as a gas, a liquid or an atomic “solid”, e.g. in a hydride compound (Schlapbach and Züttel, 2001). The energy density efficiency as seen in Fig. 1.1 (Schlapbach and Züttel, 2001) depicts the amount of storage space taken up by hydrogen in its various forms. It is obvious that the least amount of space taken up by hydrogen is in its solid state.

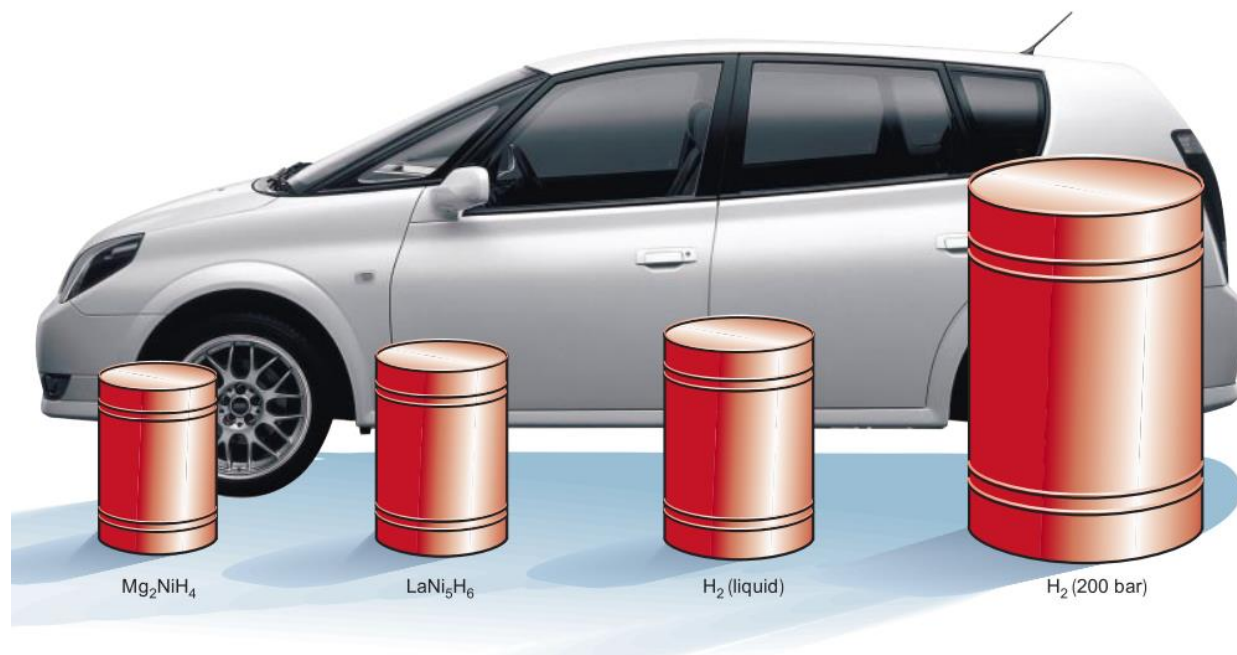


Fig. 1.1: Energy density efficiency of different storage methods (Schlapbach & Züttel, 2001)

1.2 MOTIVATION

With hydrogen being the future of sustainable energy source, it is very important to develop a process that favors economic yet generate clean hydrogen gas. The current industrial hydrogen generation method which is mainly from hydrocarbons (SMR) produces a lot of carbon dioxide as a by-product which hampers the environment. Hydrogen generation from Mg and water produces only magnesium hydroxide as the by-product. Moreover, magnesium is a very light metal and highly reactive which facilitates faster hydrogen generation. Previous studies have shown the relationship of milling time with hydrogen generation (Grosjean *et al.* 2005; Grosjean *et al.* 2004). The results were compared with the reaction of magnesium and different molar solutions of NaCl and KCl. However, a comprehensive study on the presence of the salt particles while ball-milling has not been documented. The results presented in this thesis will demonstrate the method for increasing the hydrogen yield by controlling three parameters viz.

- 1) Milling time
- 2) Type of salt
- 3) Weight percentage of salt.

The microstructural changes occurring in the Mg particles provides a deeper understanding of a role of NaCl and KCl in facilitating the reaction.

1.3 RESEARCH OBJECTIVE

- The main objective of this research is to find the most effective composition of Mg and salt sample that can produce maximum yield of hydrogen when reacted with hot water. The reaction between Mg and water depends on the structure of the Mg particle which are controlled by parameters such as milling time, type of additive and the amount of additive.
- To determine the influence of milling time on the structure of magnesium particles in the presence of NaCl and KCl for hydrogen generation.
- To determine whether the primary role of salt (NaCl and KCl) is a physical effect or a chemical effect hydrolysis (dissociation of Cl⁻ ions).
- To determine the change in the microstructure of the cross section of the ball-milled Mg particle.

CHAPTER 2

LITERATURE REVIEW

2.1 VARIOUS SOURCES OF HYDROGEN

Hydrogen can be produced by various methods. Natural gas reforming, gasification of coal and biomass, splitting of water by water electrolysis, photo-electrolysis, photobiological production, water-splitting thermochemical cycle, and high temperature decomposition are few of the many available technologies for hydrogen production. Currently, Steam Methane Reformation (SMR) is the most economical method to generate hydrogen. The other methods are not feasible for large scale hydrogen production due to high production cost.

2.1.1 Hydrogen generation from Hydrocarbons

The most common and least expensive method of hydrogen production is the SMR technique. SMR mechanism has two steps: the first step being the high temperature reaction between methane and steam at 700–1100 °C to produce synthesis gas (syngas). Syngas consists of carbon monoxide (CO) and hydrogen (H₂). During the second step, additional hydrogen is produced as CO reacts with steam.



Carbon dioxide is a by-product which is generated while producing hydrogen from hydrocarbon reforming. About 2.5 tons of carbon dioxide (CO₂) is vented into the atmosphere for each ton of hydrogen produced from reforming of hydrocarbons (US Department of Energy, 2005). Coal gasification, another conventional technology for hydrogen production also produces large quantities of CO₂ by-product. During this reaction, coal reacts with oxygen or steam to produce

hydrogen. Due to the large quantities of CO₂ emissions the use of conventional technologies for hydrogen production is less attractive. Moreover, the source for hydrogen being a non-renewable resource; it will lead to the continued depletion of fossil fuel reserves.

2.1.2 Hydrogen generation using electrolysis of water

The splitting of water to produce hydrogen is a promising process, but it is an energy intensive process using high temperatures which can be achieved only by burning fossil fuels. Various methods such as electrolysis, photocatalytic, photobiological, and thermal decomposition can be used for hydrogen production but electrolysis has the most potential. The efficiency of this reaction is highly favorable however, the cost is much higher than using fossil fuels (Ewan and Allen, 2005; Edwards *et al.* 2007).

Fortunately, electrolysis of water can be achieved using renewable resources such as solar or wind energy. It was recently mentioned by the US Department of Energy that solar photodecomposition can be a CO₂-free method of hydrogen production by splitting of water (United States. Dept. of Energy. Office of Science, 2004). The drawback of using solar energy is the land requirement, hence, modifications to solar technology are proposed. One of these modifications is the use of metal/metal oxide along with solar energy to produce hydrogen. The challenge in this process is to develop materials that can with stand high temperatures, thermal shock and oxygen while maintaining high efficiency and minimizing the reverse reaction in the first step (Vitart *et al.* 2006). The most recent advances in hydrogen production from water splitting is using nuclear energy as it is considered a good candidate for large scale production. There are various ways to use nuclear energy such as (a) electrolysis of water, (b) high temperature electrolysis using minor heat and major electricity from the nuclear reactor, (c) nuclear heated steam reforming of natural gas, and (d) thermochemical water-splitting process using major heat and minor electricity from the nuclear reactor (Kumar, 2015). Due to the societal views of using nuclear energy as a controlled energy source, the use of fission process is still under consideration. This might change in the future as nuclear energy gains acceptance as a safe energy source for sustainable power generation.

Wind energy is a source which is abundant and clean, though repeatedly challenged by low production of electrical energy. Hence, wind energy is coupled with hydrogen producing stacks of electrolyzers that will increase the efficiency of the entire process.

Even though solar and wind energy are clean sources for hydrogen production they are not sufficient to meet the global hydrogen demand. Biomass sources for hydrogen production are facing similar issues. It normally entails the conversion of a biomass to other useful products (e.g. methanol, biodiesel and pyrolysis oil) which are later be converted to hydrogen on-site. Certain types of algae are also used to produce hydrogen; they split water into its constituents in bioreactors (Melis and Happe, 2001). In the last 25 years, CO₂ emissions due to hydrogen generation have been reduced by 20%, but this is not enough. A lot more needs to be done to further reduce this figure (Bonaquist, 2010), hence there is an urgent need for clean technologies for hydrogen production.

2.1.3 Hydrogen generation from reaction of metals with water

Metals such as zinc, Mg and Al when react with water produce hydrogen. These metals are even mixed with various catalysts to improve the reaction. Successful tests have been conducted using these three metals for hydrogen generation, they all react with water to produce metal oxides and hydrogen gas. There are fewer reports available in the literature for zinc compared to Mg and Al (Funke *et al.*, 2008; Berman and Epstein, 2000; Weiss *et al.* 2005).



Funke *et al.* (2008) investigated the reaction of zinc nanoparticles with water vapour, and observed inherent hinders due to the formation of ZnO films (Funke *et al.*, 2008). A. Berman *et al.* have reported that the kinetics of this reaction depends on rate at while these oxide layers are formed (Berman and Epstein, 2000). Moreover, zinc (65.5g) is a heavier metal compared to Mg (24g) and Aluminum (27g), and one mole of zinc produces one mole of hydrogen which means hydrogen produced per unit mass of zinc is much less compared to Al and Mg



Aluminum and Mg are the two metals to which a lot of studies have been conducted, this is due to abundances and considering that these metals are more reactive in water. Mg also has an advantage of being the lightest metal of the three. Previous studies have discussed hydrogen generation from

Mg and Mg alloys upon reaction with water (Equation 2.4) (Grosjean *et al.* 2005). Grosjean *et al.* (2006) have also reported a hydrogen production process by means of Mg/MgH₂ powders ball-milling with different salts (e.g. KCl, NaCl, LiCl, MgCl₂). The morphologies of these refined powders after 30 mins milling period are presented in Fig. 2.1. Fig. 2.2 shows the effect of addition of salt while ball milling Mg for the same duration of time. The addition of 10 mol% of KCl in the mixture accelerates the process of particle size reduction. The maximum hydrogen yield of 55% was obtained from 10 mol% KCl.

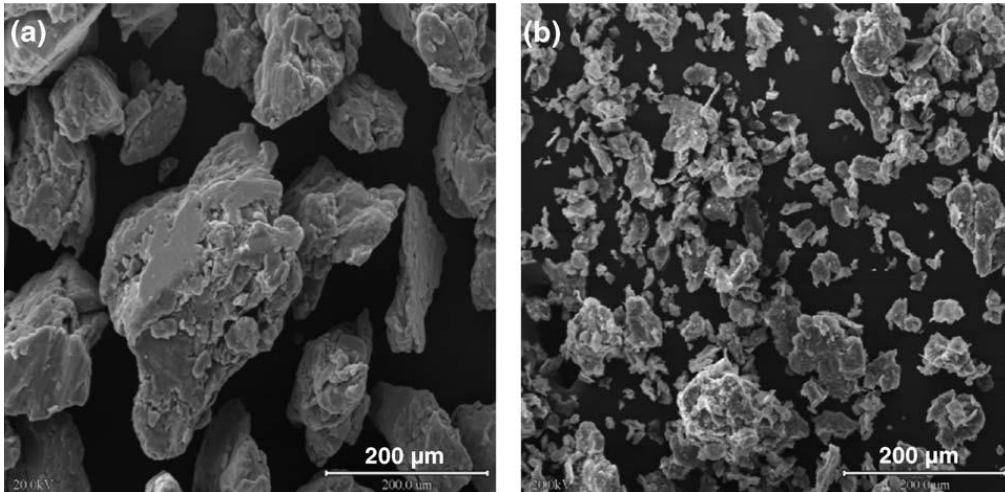


Fig. 2.1: SEM micrographs of (a) Mg powder and (b) Mg-10 mol% KCl mixture obtained after 30 min of milling (Grosjean and Roue, 2006).

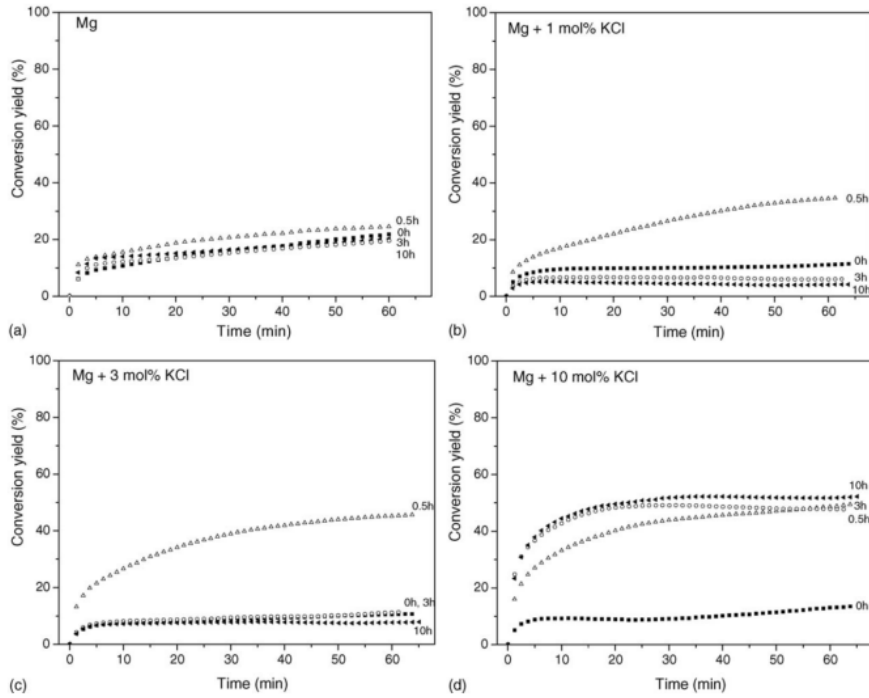


Fig. 2.2: Hydrogen generation graphs for reaction with water of (a) Mg, (b) Mg–1mol% KCl, (c) Mg–3mol% KCl and (d) Mg–10mol% KCl powders milled for different times (Grosjean & Roue, 2006)

In another experiment by Grosjean *et al.* (2005), the hydrogen yield for different combinations of milling time for pure Mg and MgH₂ in combination with pure water and 1 M KCl solution is presented in Fig. 2.3 for different time durations. Here KCl is used in its aqueous state during hydrolysis. Grosjean *et al.* (2005) also claims that the effect of KCl as a solution instead of ball milled along with Mg produces a better yield of hydrogen due to pitting corrosion.

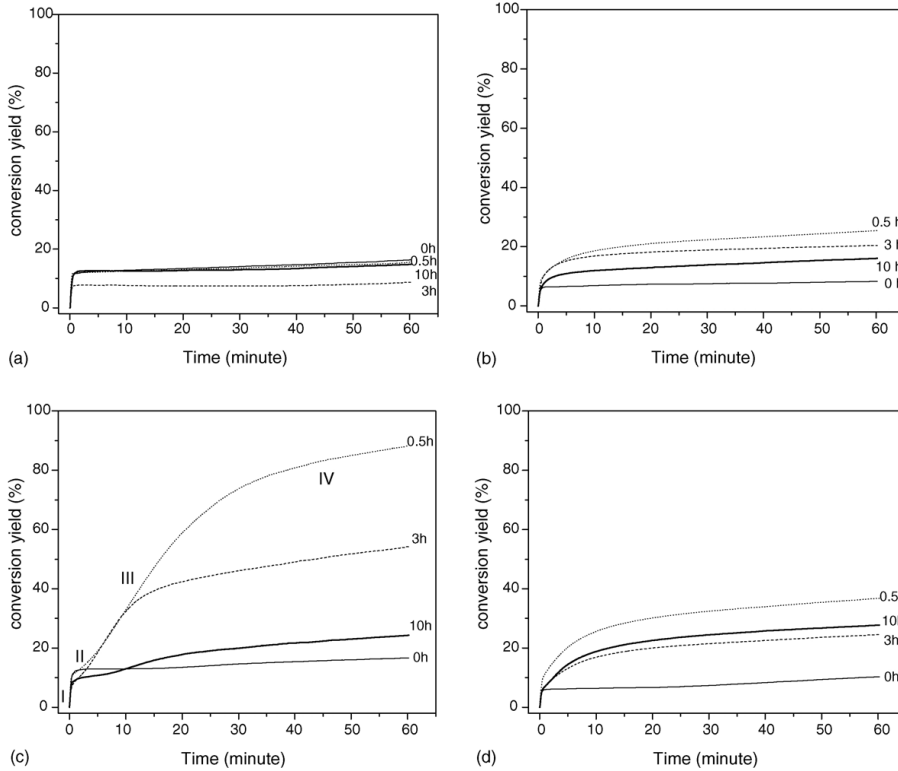


Fig. 2.3: Hydrogen production curves of (a) Mg in pure water, (b) MgH₂ in pure water, (c) Mg in 1M KCl, (d) MgH₂ in 1M KCl for different milling times (0,0.5, 3 and 10 h) (Grosjean *et al.*, 2005).

Previous researches have focused on improving the conversion yield for hydrogen production (Grosjean *et al.* 2004, Grosjean *et al.* 2005, Grosjean and Roué, 2006). However, reaction kinetics is not the only criterion that is important for an acceptable energy carrier. One should consider that cost of produced hydrogen via Mg-water reaction should be minimized. Also, the microstructure of the cross section of the particles was not examined. Ball milling Mg with additives such as NaCl and KCl increase the hydrogen yield and are good as they are cheap plentiful and safe. The reaction rate and conversion yield depend on the amount of additives, size and composition of additive powders and milling condition. Such parameters should be optimized for an increase in yield/rate of reaction and this has not yet been done. There are not enough studies considered how such parameters can be modified to obtain the best possible results. Section 4.1 and 4.2 discusses the change in microstructure of pure ball milled Mg and the microstructure of Mg particles when ball milled with NaCl. The effect of ball milling time on the microstructure with and without the presence of NaCl are also documented. The effect of the microstructural changes on the hydrogen yield is important as this is evident from the results presented in section 4.2.1.

2.2 STRUCTURAL MODIFICATION OF METAL PARTICLES BY BALL MILLING

High energy ball milling was initially used by John Benjamin as a method for production of oxide dispersion strengthened (ODS) alloys (Benjamin & Volin, 1974). Since then, this method has been extensively used for production of nanocomposites, nanostructured materials, metal matrix composites and synthesis of new materials (Suryanarayana, 2001). The various types of mills for high energy milling used today are planetary ball mill, Attritor and SPEX. The planetary ball mill is the most popular for lab researches.

As the name suggests, a high energy milling method applies a high amount of energy to the particles compared to conventional milling (Suryanarayana, 2001). This helps in achieving the final product in a short duration of time. On the other hand, the high energy ball mill requires a very high electrical energy to run which adds to the final price of the product.

Researchers have adopted two ways to decrease the energy needed for production of powder products by high energy mills, the first being able to find the steady state time which is the minimum time needed to produce the desired products. Steady state time is also defined as the milling time after which further milling has negligible effects on the powder products (Benjamin and Volin, 1974; Fogagnolo *et al.* 2006; Fogagnolo *et al.* 2003; Suryanarayana, 2001). Steady state can be determined by considering the criteria such as change in shape of the particles, orientation and presence of lattice imperfections of the particles

The second method of decreasing the energy consumed by high energy mills is by reducing the milling time by making suitable change in ratio of rotation of vials compared to disk (Mio *et al.* 2004; Mio *et al.* 2002), balls size (Ward *et al.*, 2005; Sato *et al.* 2010; Ma *et al.* 2009; Kano and Saito, 1998; Watanabe *et al.* 1995), mill speed (Ashrafizadeh and Ashrafizaadeh, 2012; Dallimore and McCormick, 1996; Iasonna and Magini, 1996; Kano and Saito, 1998; Magini *et al.* 1998; Magini and Iasonna, 1995; Mio *et al.* 2002; Mio *et al.* 2004; Sato *et al.* 2010), filling ratio of vials (Ashrafizadeh and Ashrafizaadeh, 2012; Iasonna and Magini, 1996; Magini *et al.* 1998; Rosenkranz *et al.* 2011; Sato *et al.* 2010; Ward *et al.* 2005; Watanabe *et al.* 1995) and charge ratio (Delogu *et al.* 2003; Jiang *et al.* 2009; Murty *et al.* 1995; Ward *et al.*, 2005). All these factors have been studied to optimize the milling process. While there is no concrete evidence on the effect of these variables, researchers have concluded that a higher milling speed and a larger charge ratio helps to achieve the final product faster. Nevertheless, a higher milling speed means higher power

consumption and a larger charge ratio means less amount of the final product. These factors increase the final price of the product though the time taken to obtain the final product is reduced. The microstructural changes during ball milling for ductile metals like Mg are explained by two mechanisms namely cold welding and fracture. Cold welding occurs initially when ball milling commences. This is because the particles are ductile initially. As milling continues fracture mechanism takes over as work hardening occurs in the microstructure (Fogagnolo *et al.* 2006; Fogagnolo *et al.* 2003; Razavi Tousi *et al.* 2009). The steady state time for a single phase ductile metal is defined as the time interval after which cold welding and fracture process reach an equilibrium. The particle size does not change once steady state time is reached. Fig. 2.4 shows the schematics of ball and particles during ball milling.

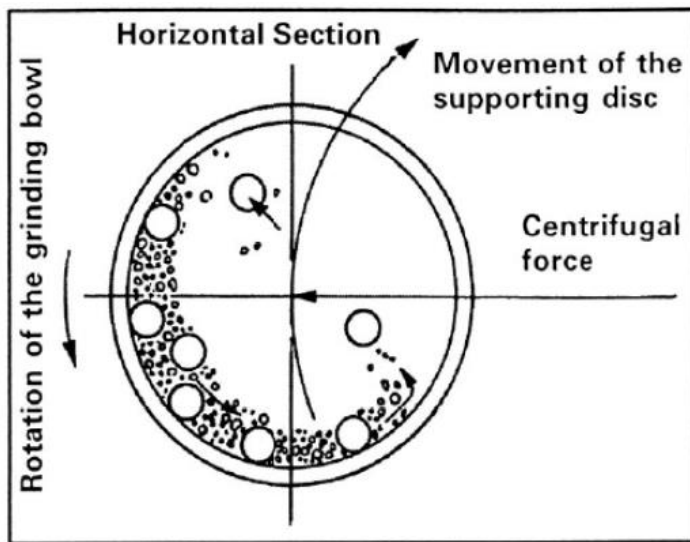


Fig. 2.4: Schematic showing ball and particles in a vial in planetary ball mill (Suryanarayana, 2001)

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 MATERIALS

The Mg powder deployed within this work was purchased from Alfa Aesar (particle size: -20+100 mesh; purity: 99.8%). Other chemicals include sodium chloride (99% purity) and potassium chloride (99% purity); they served as process control agents.

3.2 METHODOLOGY

3.2.1 Ball milling of Mg powder

After mixing sodium chloride with the Mg powder, the mixture was ball milled for different weight percentages of NaCl (25%, 50%, 75%). Ball milling was performed on a planetary ball mill Fig. 3.1 (Torrey Hills- ND2L) with a BMR of 30:1 in inert argon atmosphere. The inert gas prevented oxidation and prevented magnesium from reacting with air by catching fire. The milling speed was maintained at 200 rpm for durations of 1, 3, 7 and 15 h to evaluate the effect of the milling time on microstructure. To assess the influence of type of salt, mixtures of 25 wt% KCl- 75 wt% Mg, 75 wt% KCl- 25 wt% Mg and 50 wt% KCl- 50 wt% Mg were also ball milled for durations of 1, 3, 7 and 15 h.



Fig. 3.1: Torrey Hills- ND2L ball milling equipment

3.2.2 Hydrogen generation by reaction of Mg powder with hot water

Powdered mixtures of Mg were added to an Erlenmeyer flask containing 200 ml of distilled water at 80 ± 2 °C at a constant stirring rate of 120 rpm. The evolving gaseous (hydrogen gas) produced was passed through a desiccant (CaSO_4) to absorb moisture, and then to an ADM1000 flowmeter to measure its flow rate. The flowmeter was connected to a computer running ADM Trend software to acquire the data. The hydrogen yield curve was obtained by integrating the flow data over time. Some of the measurements were repeated in order to ensure the results obtained were reproducible.

The hydrogen flow measurement was not continued after 60 min as the obtained data was enough to investigate the effect of microstructure on the rate of Mg+NaCl-water reaction. The flow was

then normalized for 1g Mg powder. Fig. 3.2 shows the set-up and a flowchart of hydrogen measurement.

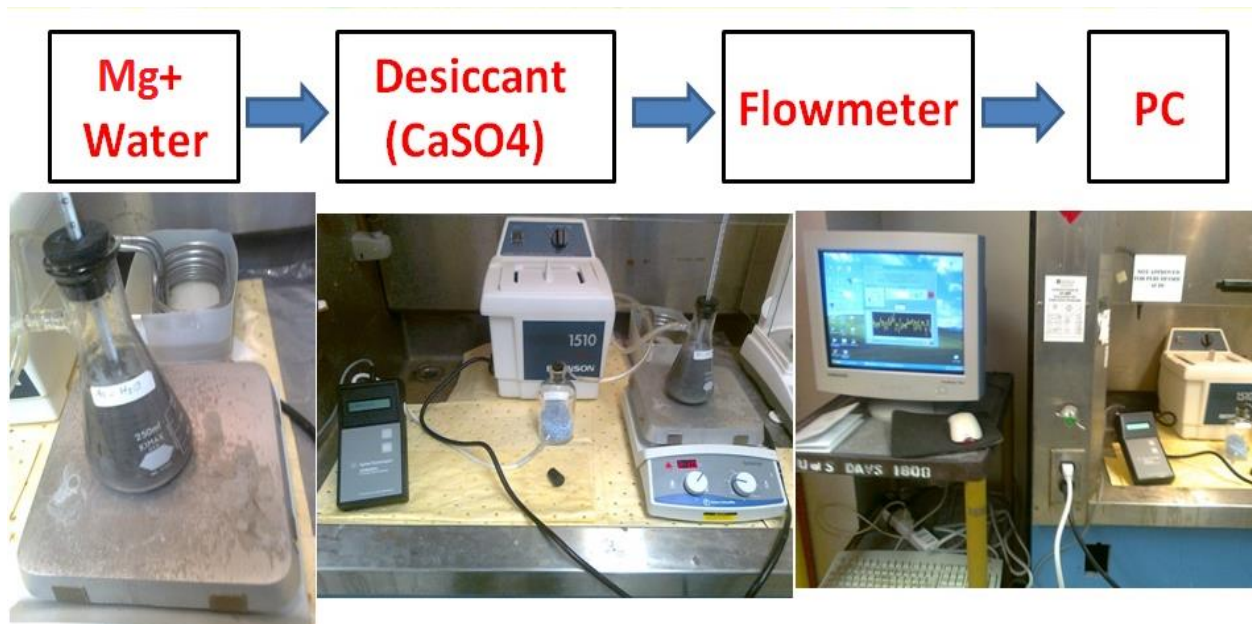


Fig. 3.2: Layout of the hydrogen measurement apparatus

To make sure that water moisture or expansion of air in the flask during heating was not measured with the hydrogen flow, a baseline curve Fig. 3.3 was subtracted from the flow obtained from the reactions. This background reading (baseline curve) was obtained by measuring the flow from 200 ml distilled water at temperature of 80°C with a constant stirring rate of 120 rpm with no Mg powder added. From Fig 3.3 the baseline curve was calculated as 0.56 ml/min.

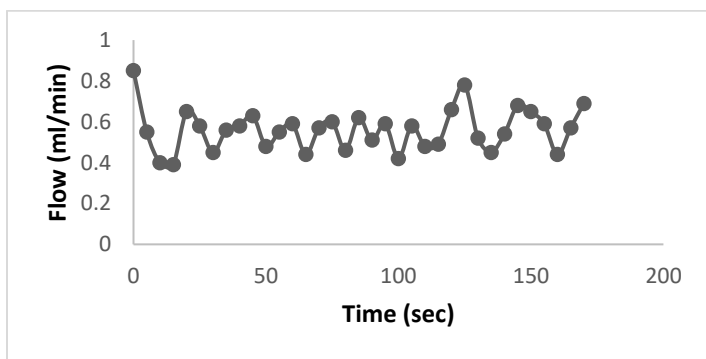


Fig. 3.3: Background reading from the flowmeter which was subtracted from the reading

3.2.3 Examination of deformed particles on scanning electron microscopy

SEM examinations were made using Hitachi SU6600 field emission scanning electron microscope. Prior to SEM analyses, the Mg particles were first dispersed on a double sided black conductive tape. For the cross section of the particles, a small amount of each ball-milled powder was mixed with a conductive carbon resin powder mixed and mounted. The mounted samples were then polished using abrasive grinding papers ranging from 600 to 2000. The polishing medium used was ethyl alcohol instead of water based medium as the salt (NaCl and KCl) in the samples have a very high tendency to dissolve in water and also oxidizes the Mg particles. Ethyl alcohol stops oxidizing of Mg and prevents the dissolution of salt. Average particle sizes of the mixture were calculated using ImageJ software.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EFFECT OF BALL MILLING TIME ON THE MORPHOLOGY OF AS RECEIVED MAGNESIUM

Pure Mg was ball-milled in order to study the changes within the particulate structure when milled at different periods. This procedure aided a better understanding of fragmentation and cold-welding processes occurring during ball milling. As ball-milling mechanism is different for different metals, Mg being a ductile metal would not fracture easily. Hence the maximum time after which ball milling did not have an effect on particle size was noted. This time is set as the steady state time. Prior to this, the pure Mg powdery particles were smooth and oblong in shape as shown in Fig 4.1, with an average particle size of 0.8 mm. Ball-milling was then conducted in the presence of argon atmosphere in order to prevent oxidizing and combustion. When the milling time was varied between 1 h and 15 h, significant morphological changes were observed. The mechanism of ball milling as discussed earlier occurs with the combination of cold welding and fracture. This result explains that particles after 1 hour of milling reduced by almost half their initial sizes as seen in Fig 4.2. The region of cold welding is indicated in the enlarged micrograph represented by arrows in Fig. 4.2. This process of gradual size reduction was observed for the particles milled for 3 hours as presented in Fig. 4.3. The evenness of particulate morphologies is unchanged with size reduction. As milling continued to 7 hours (Fig. 4.4), drastic reduction in the average particulate size and morphological changes are observed. The particles observed in Fig 4.4 are flat-plate like structures due to inherent fracture process that took place during cold-welding.

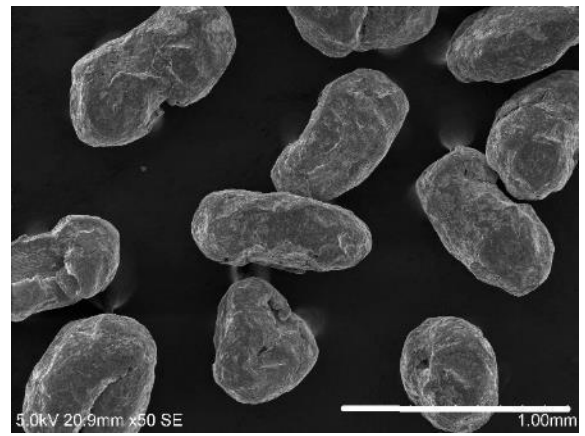
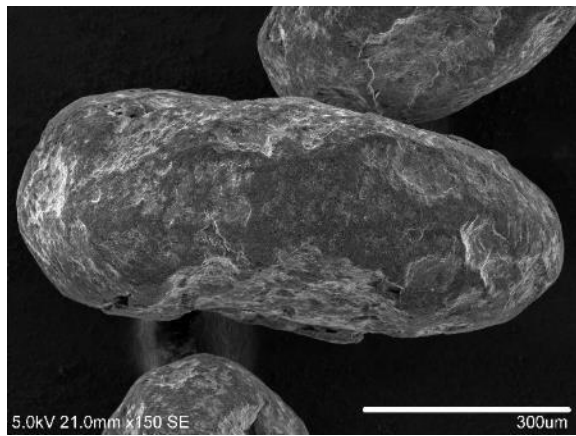


Fig. 4.1: Morphology of as-received Mg powder

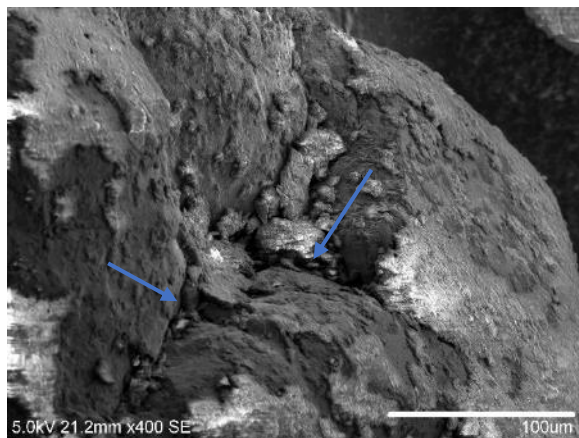
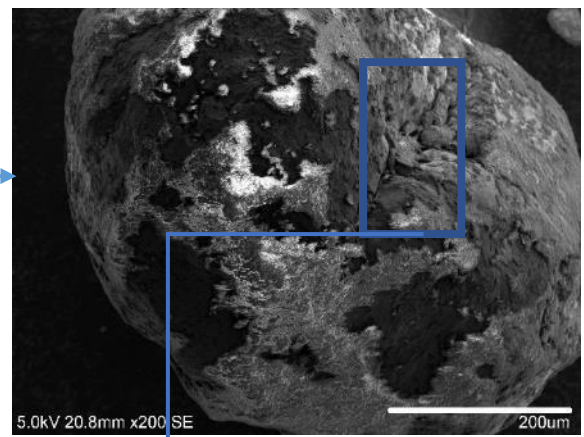
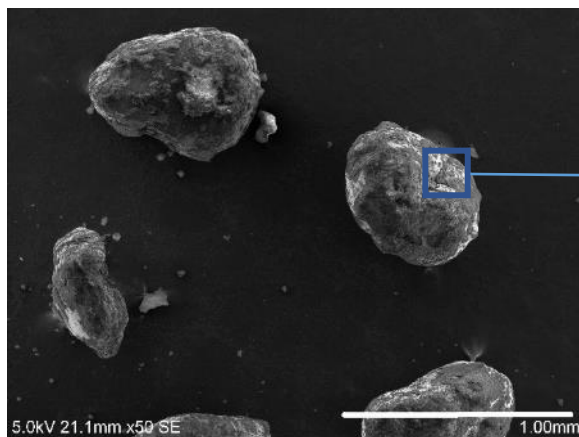


Fig. 4.2: SEM images of pure Mg powder ball-milled for 1 h.

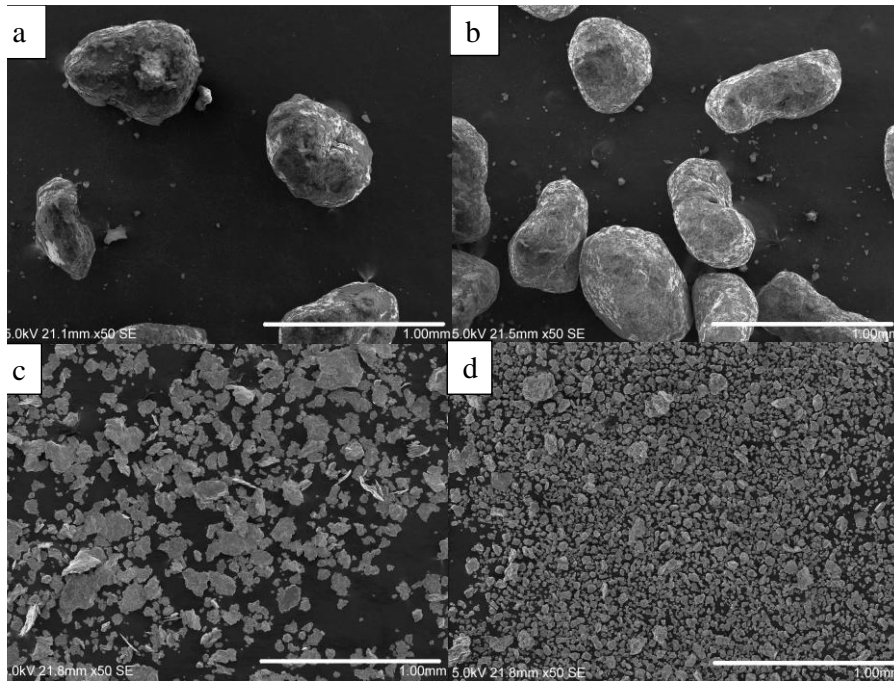


Fig. 4.3: Morphology of pure Mg powder ball-milled for (a) 1 h (b) 3 h (c) 7 h (d) 15 h

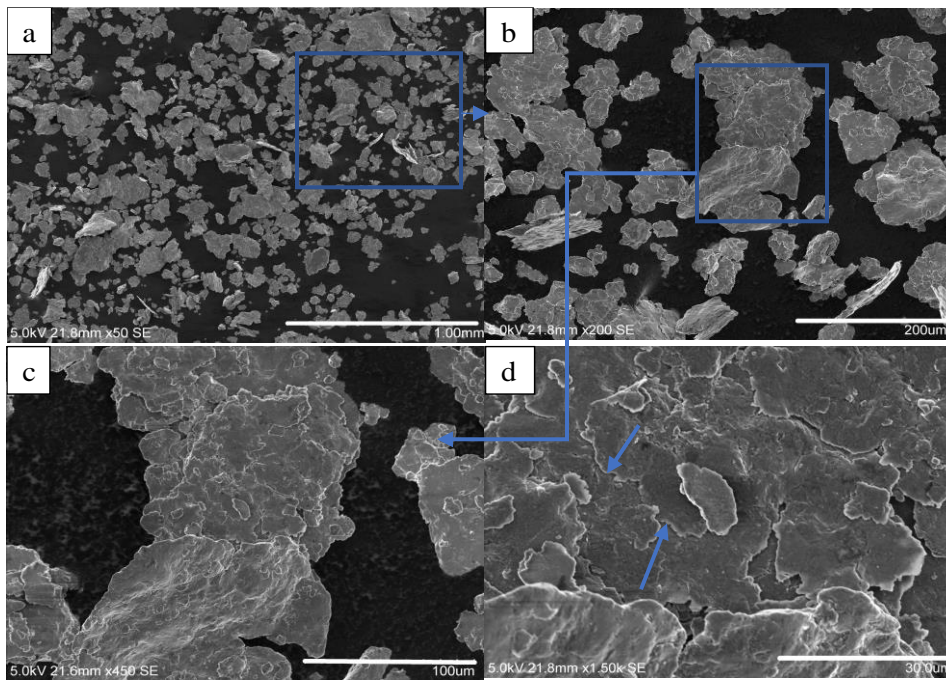


Fig. 4.4: SEM images of pure Mg powder ball-milled for 7 hr. Note the change in scale

As discussed in the ball-milling procedure, the steady state for a ductile metal is defined as a state when equilibrium is reached between cold welding and fracture. The particulate morphology in Fig.4.5, after 15 h milled period is an evidence of the equilibrium state reached between fracture and cold welding. The particles are round with relatively similar shapes as those revealed after 1h and 3h milled periods except for the thin laminated surface structures. In all, the effect of milling time on pure Mg particles helps us understand the mechanism of milling process and also helps us determining the steady state time.

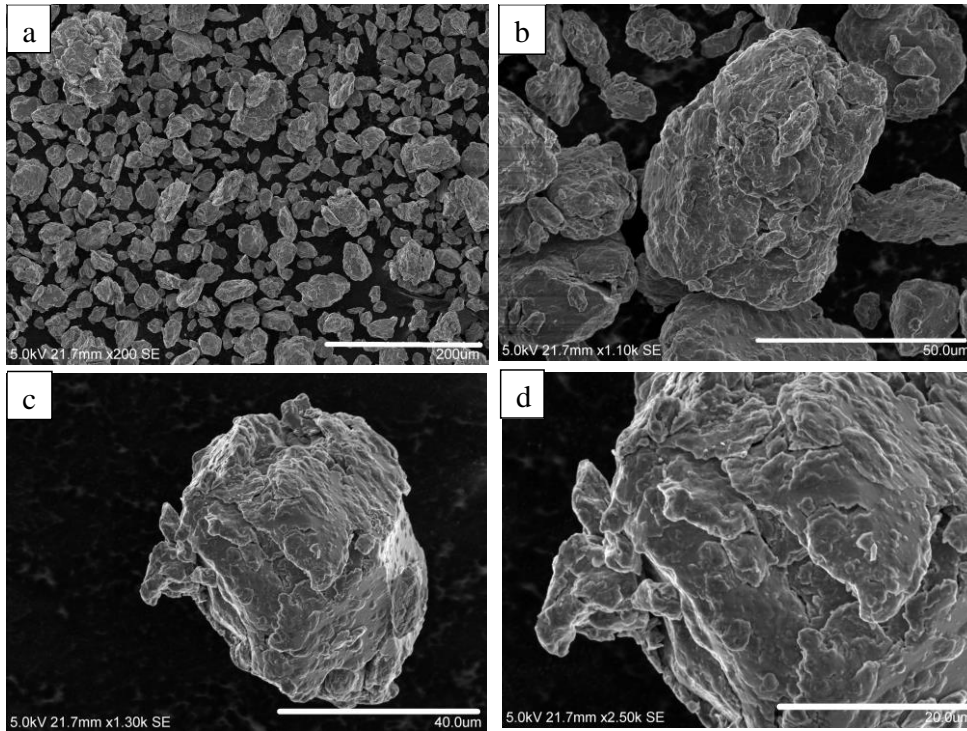


Fig 4.5: SEM images of pure Mg powder milled for 15 h.

4.2 EFFECT OF MILLING TIME WITH NaCl SALT ON HYDROGEN GENERATION

4.2.1 Hydrogen measurement for milled Mg 50%-NaCl 50% mixture

Milled Mg (pure) powder did not show any hydrogen generation. This could be because of the oxide layer forming on the surface of the particles. Another reason was that the magnesium powder was difficult to wet making it float on the water. The as-received and non-milled Mg and NaCl powder without ball milling also failed to generate the gas. Fig. 4.6 shows the quantity of hydrogen generated from milled Mg-NaCl (1:1 equimolar ratio) mixtures at different time periods in hot water at 80 °C; results are normalized for 1 g Mg powder.

An amount of hydrogen below 100 ml has been produced from the binary mixture milled for 1 h. Significant increase is observed after 3 h (300 ml) and for 7 and 15 h durations, respectively. The theoretical hydrogen generation maximum for 1 g of Mg with water is 930 ml.

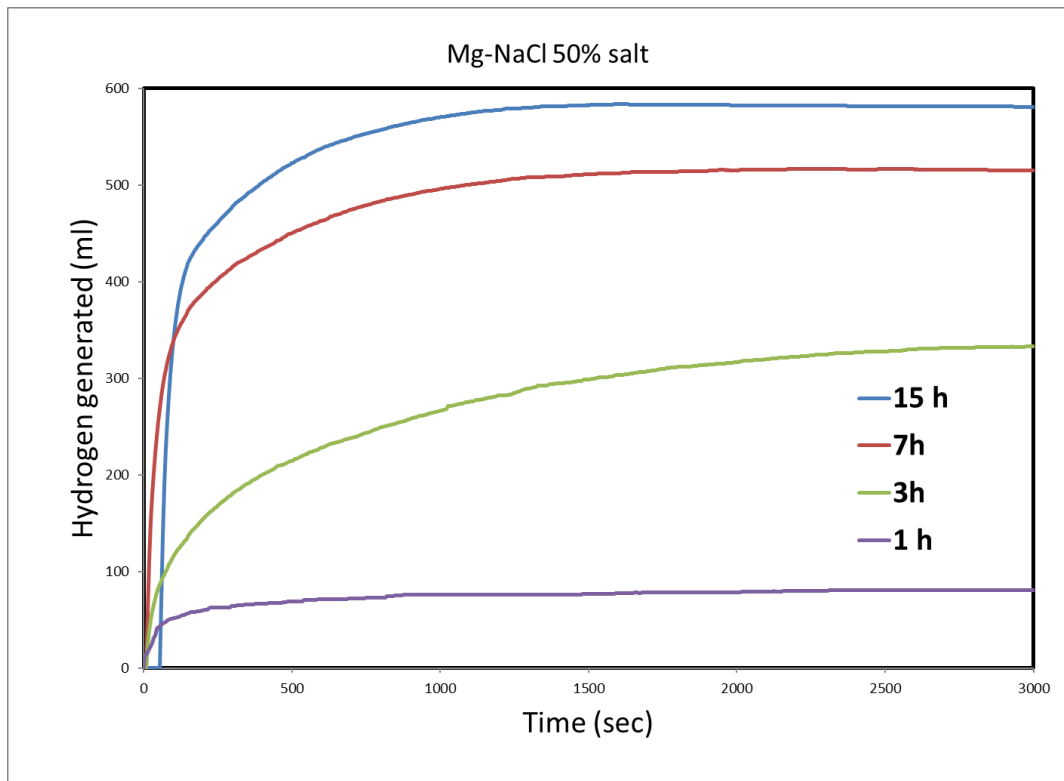


Fig. 4.6: Hydrogen generated for Mg 50%-NaCl 50% mixture for 1 h, 3 h, 7 h and 15 h milling period

Further milling of the mixture to 25 h and 50 h resulted in cold welding of Mg particles and were extremely reactive, hence were not fit for hydrolysis.

As these results state that no hydrogen was produced with pure ball milled Mg nor with the as received Mg and NaCl mixture (which was not ball milled); the fact that NaCl alone is not effective in hydrogen generation nor is it effective when it is not present during milling brings us to the conclusion that the presence of salt during ball milling plays an important role and secondly the presence of Cl^- ions does not play a significant role in pitting corrosion of Mg in such a short reaction time (1h) in contrast to what was suggested to Grosjean et al (2006).

The hydrogen generation in Fig 4.6 shows that the hydrogen generation increases with increasing milling time for Mg-NaCl mixture.

4.2.2 Microstructure of ball-milled Mg 50%-NaCl 50% mixture

The milled mixture was examined by SEM in order to understand the mechanics behind improved hydrogen generation with milling time. The micrographs are presented in Fig 4.7, revealing characteristic changes in particulate morphology and sizes after milling. After 1 hour, the Mg particles which were initially spherical are deformed to form flat disk structures with an average particle size of 690 μm . Further milling deforms the particles until a point of fracture is reached and smaller particles are formed. The average particle size of Mg which was ball milled for 3 h, 7 h and 15 h is 277 μm , 65 μm and 46 μm respectively. From XRD analysis there was no evidence that the reaction between Mg and NaCl takes place as reported by Grosjean et al. (Grosjean & Roue, 2006).

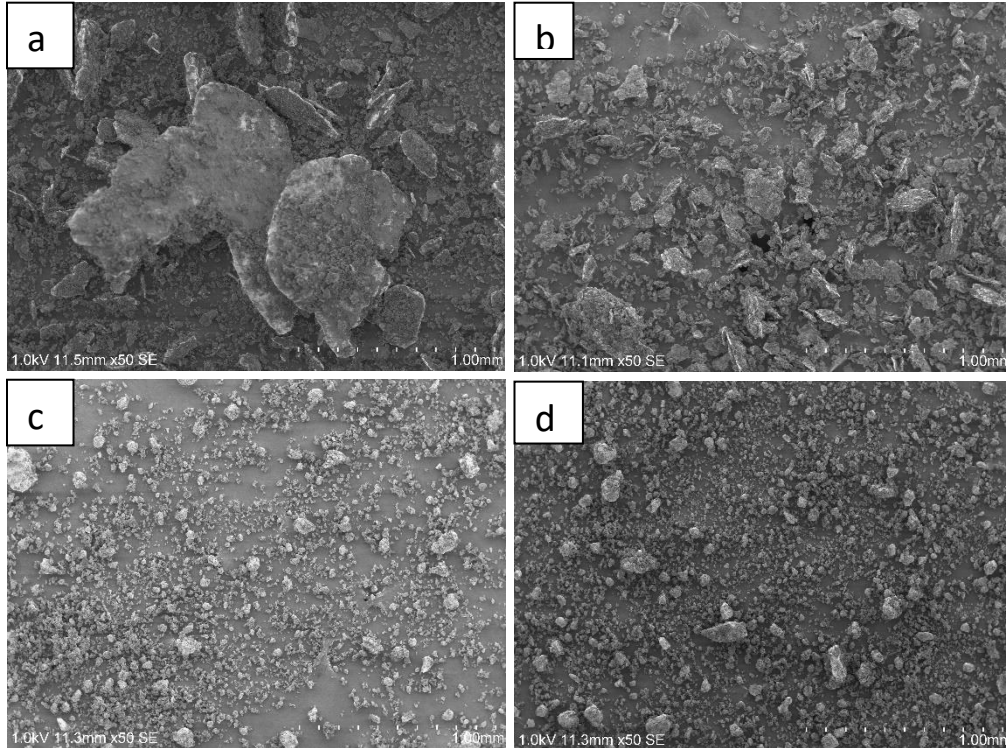


Fig. 4.7: SEM images comparing the Mg 50%-NaCl50% mixtures milled for 1h, 3h, 7h, and 15h

As seen earlier from Fig 4.6, the highest hydrogen generation rate was obtained for 15 h milled mixture (Mg50%-NaCl50%) which shows that higher milling time enhances hydrogen production. During hydrolysis process, hot water comes in contact with the surface of Mg particle, and milling

Mg with NaCl allows NaCl particles to get embedded in the Mg particle. During the reaction NaCl dissolves in water leaving voids and tunnels in the Mg particle. This increases the surface area of Mg which is in contact with water. For higher milling times, we see an increase in hydrogen generation as NaCl is embedded deeper as milling time is prolonged. This results in higher porosity of Mg as the salt dissolves in water which in turn increases the specific surface area.

The EDS scans in Fig 4.8 show the distribution of Mg and NaCl particles. The green represents Mg while Na is mapped red. For the mixture milled for 1 h, NaCl is seen covering the surface on the Mg particles. As the milling time was increased to 3 h, there were still some dark spots observed on the Mg particles which corresponded to NaCl. Further milling for 7 h and 15 h shows a homogenous distribution of both Mg and NaCl phases. This shows that the particle is Mg-NaCl composite in which the two phases occur so closely to each other that they cannot be distinguished by the EDS detector.

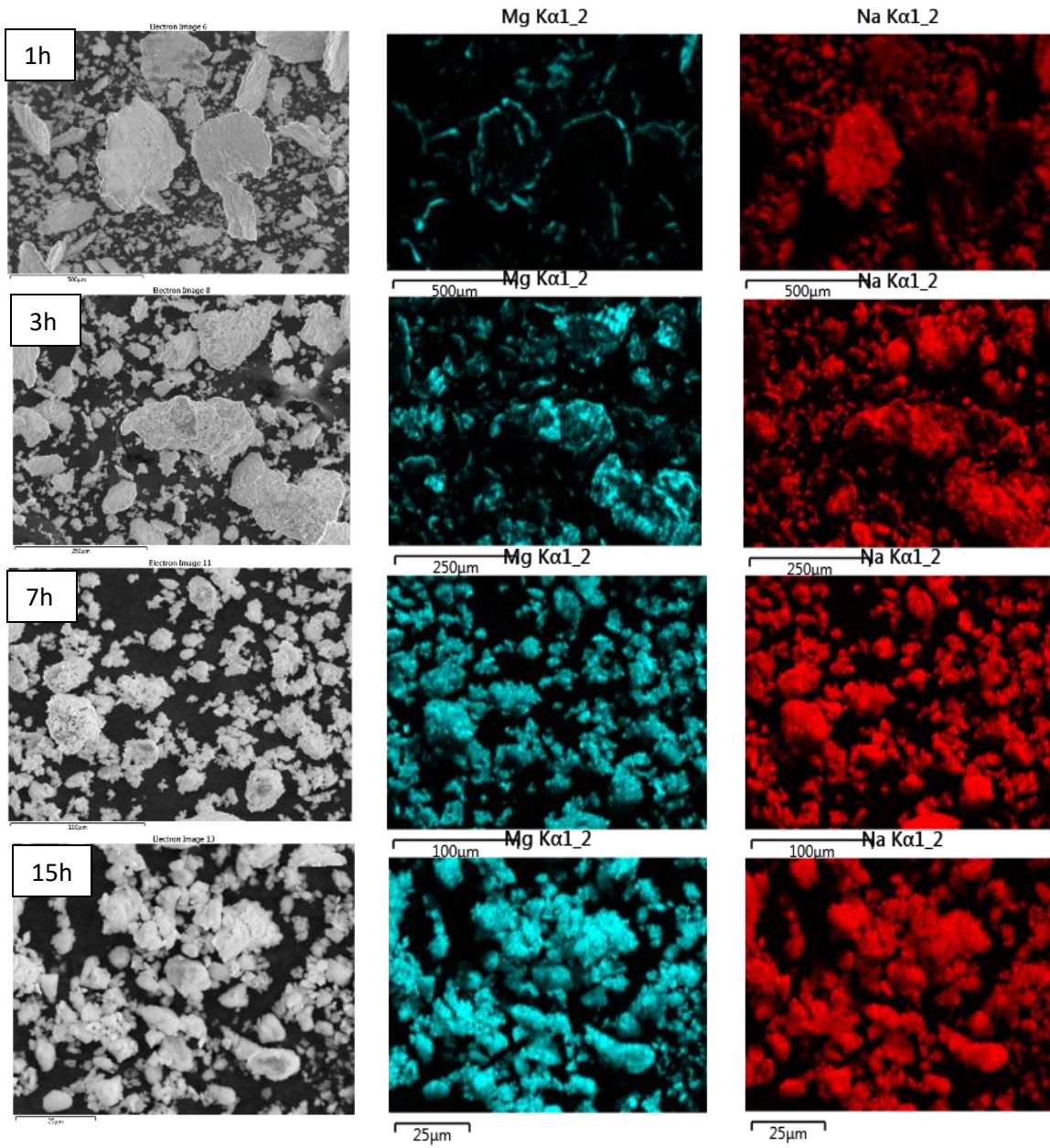


Fig. 4.8: Elemental mapping of mixture showing the homogeneity of Mg and NaCl for different ball milling times

Fig. 4.9 represents the elemental maps of the cross section of Mg50%-NaCl150%; NaCl did not penetrate deep within Mg for 1 h milled particles. The embedding of NaCl helps create voids when dissolved in water thus creating fresh surface for hydrolysis. The presence of some amount of NaCl is revealed in the cross section of 3 h milled mixture.

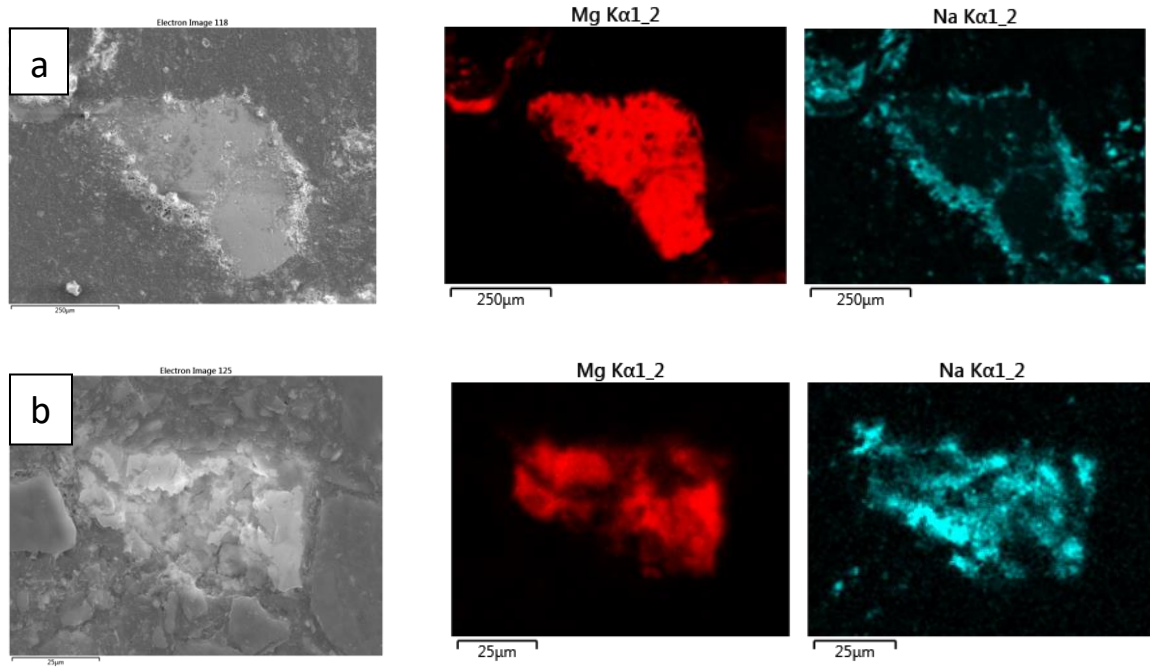


Fig. 4.9: EDS scan of cross section of Mg50%-NaCl150% mixture ball milled for a) 1h b) 3h

Comparing EDS scans in Fig. 4.9 and Fig. 4.10, the extent of NaCl that has been able to embed in the Mg particle is revealed. Fig. 4.9 shows areas for Mg and NaCl which were ball milled for 1 h and 3 h. For the samples in Fig 4.10 which were ball milled for 7 h and 15 h there is no clear distinction between the Mg and NaCl phase which means Mg and NaCl are homogeneously distributed.

Further increasing the milling time above 15 h resulted in cold welding as all the NaCl on the surface were embedded in the Mg matrix leading Mg particles. This illustrates the importance of ball milling Mg-NaCl.

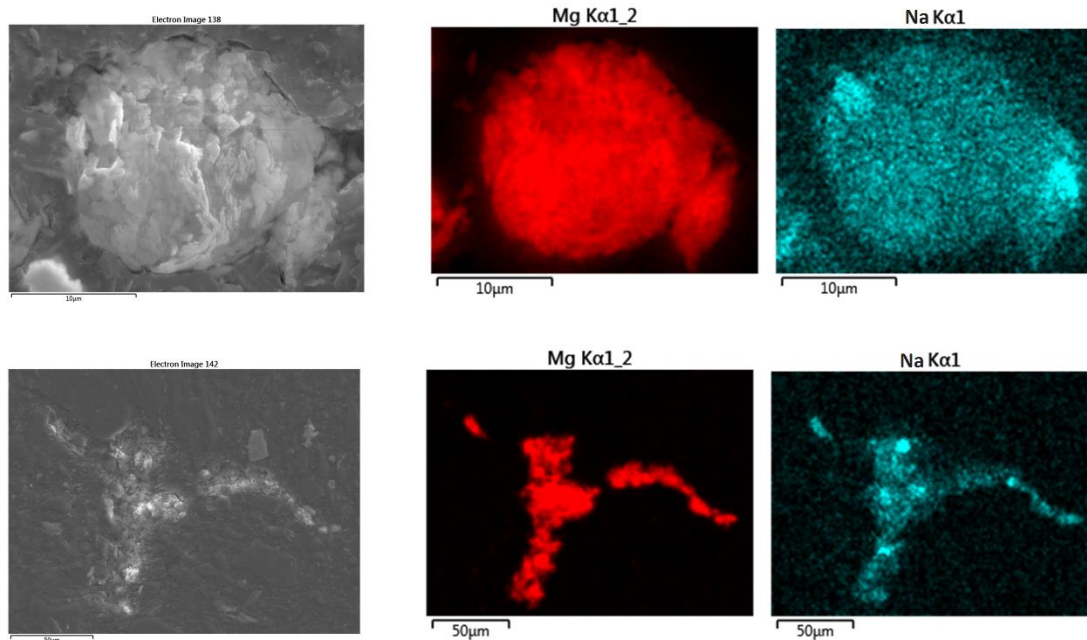


Fig. 4.10: EDS scan of cross section of Mg-NaCl mixture ball milled for a) 7 hr b) 15 hr

The EDS line scan in Fig 4.11 reveal the presence of Mg and NaCl for 1 h, 3 h, 7 h and 15 h milled mixtures; the red line represents Mg while Na is mapped violet. These scans were obtained across the cross section of a particle and they represent the occurrence of both elements. For shorter milling times (1 h and 3 h) the signals from Mg and NaCl are not overlapping and as milling time increased (7 h and 15 h) the presence of Mg and NaCl is registered in the same area. This validates the results from EDS maps which show that increasing milling time leads to a homogenous distribution of Mg-NaCl segments.

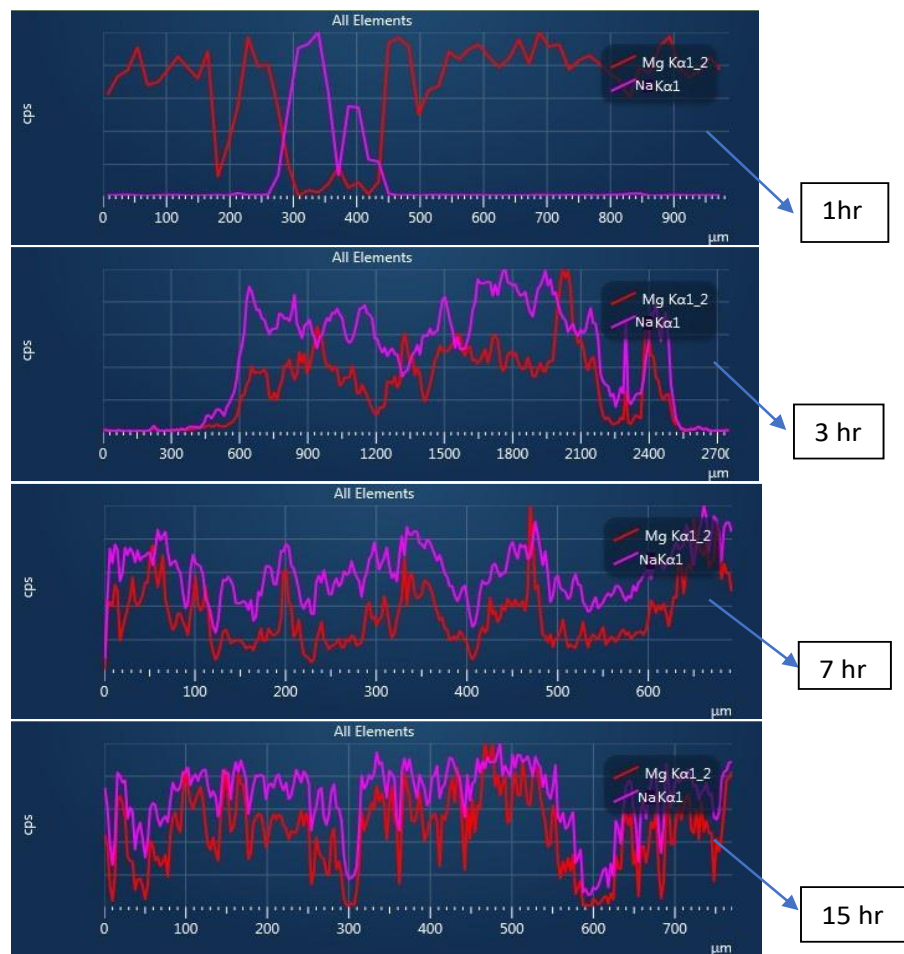


Fig. 4.11: Line scan showing the occurrence of Mg and NaCl on the cross section of the particle for different ball milling time

In a discussion of chemical processes which might be involved Grosjean *et al.* states that in the aqueous form Cl^- ions destabilizes the OH^- ions in magnesium hydroxide which then form a soluble MgCl_2 which in turn increases the hydrogen yield. (Grosjean and Roue, 2006).

However, as for our result the molar ratio of Mg and NaCl (Mg50%-NaCl50%) is fixed and so the presence of Cl^- would produce the same chemical effect. The only change present is the structural change in Mg particle which was due to the change in milling time. This suggests that the chemical effect of the Cl^- ions is negligible compared to the structural effect.

4.3 INFLUENCE OF WEIGHT PERCENTAGE OF NaCl ON HYDROGEN GENERATION

This section highlights the changes in weight percentage of NaCl (25%,50%,75%) within Mg-NaCl mixture and how this percentage affects hydrogen generation and microstructure of Mg particle. Fig. 4.12 and 4.13 show trend of hydrogen generation from milled Mg-NaCl 25% and Mg-NaCl 75% composites at different time durations (1 h, 3 h, 7 h and 15 h) for 1g Mg. It is evident that the amount of hydrogen generated is higher for a higher percentage of salt content within the composite. Comparing hydrogen generation profiles from Fig. 4.6, Fig. 4.12 and Fig. 4.13, for the same time period of milling, amount of hydrogen generated is higher for higher percentage of salt.

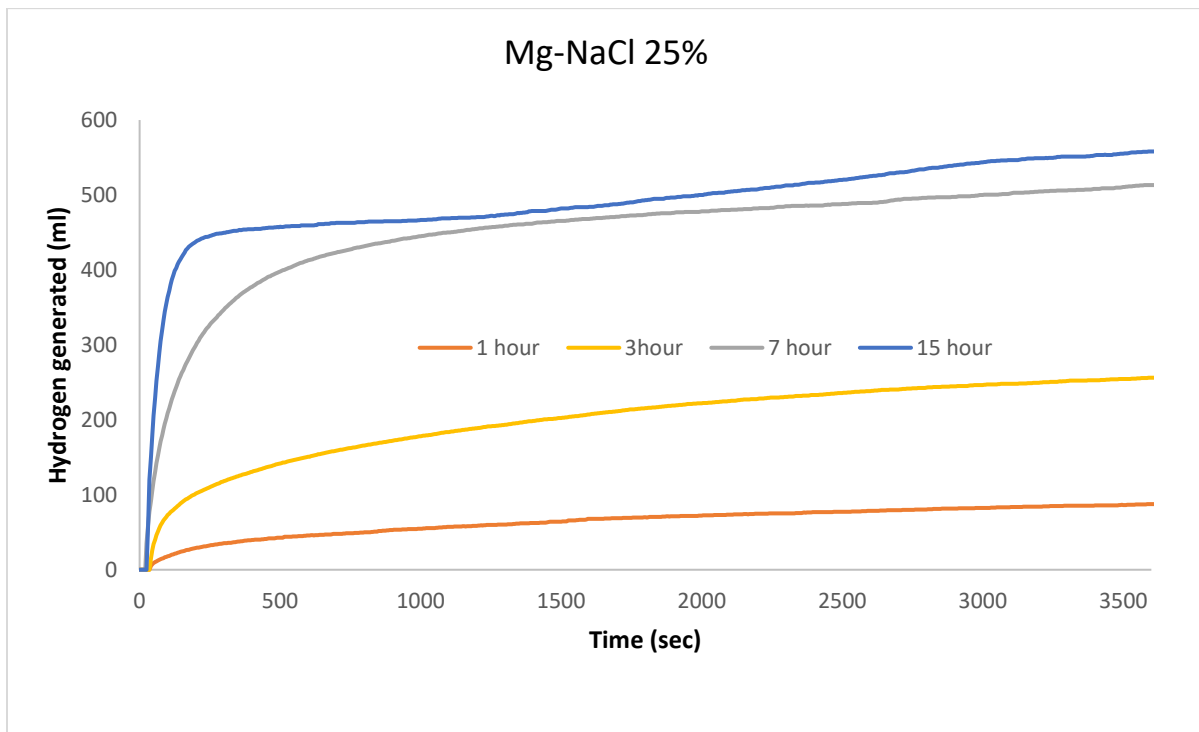


Fig. 4.12: Hydrogen generation profile for Mg 75%-NaCl 25% mixture ball-milled for 1 h, 3 h, 7 h, 15 h.

Maximum amount of generated hydrogen was for 15 h for Mg-NaCl 75% mixture (900ml) and this amount is relatively close to the theoretical value for 1g Mg. The increase in produced hydrogen is due to the formation of pores within Mg that are filled by NaCl that gradually dissolves

in water. This leads to an increase in the specific area of Mg in contact with water which explains the improved kinetics of the reaction.

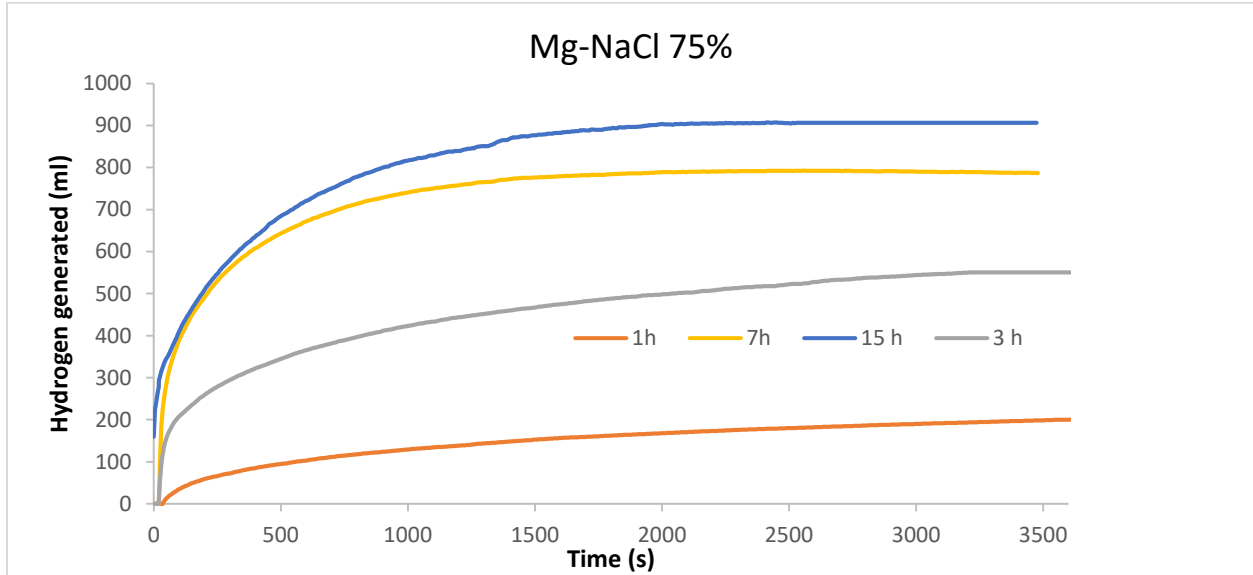
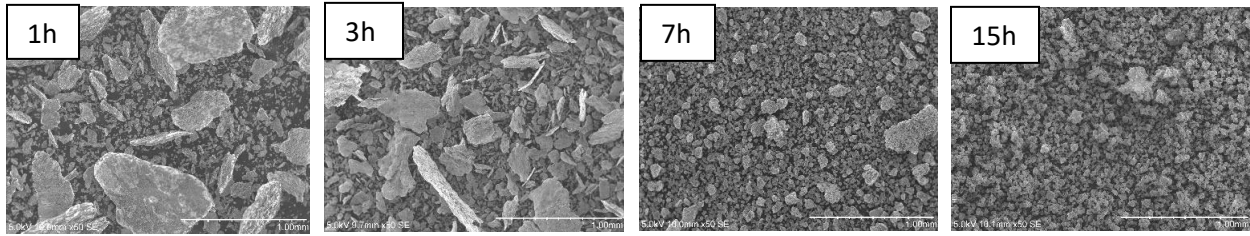


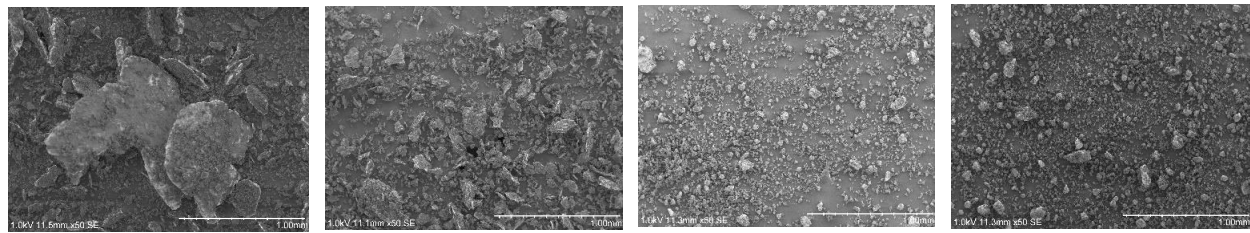
Fig. 4.13: Hydrogen generation profile for Mg 25%-NaCl 75% mixture ball-milled for 1 h, 3 h, 7 h, 15 h.

The SEM micrographs in Fig 4.14 illustrate a decrease in average particle size as the wt% of NaCl increase while the milling time is constant. This can be explained by the role of NaCl in preventing cold welding of Mg particles (Marie Helene Grosjean & Roue, 2006).

NaCl25



NaCl50



NaCl75

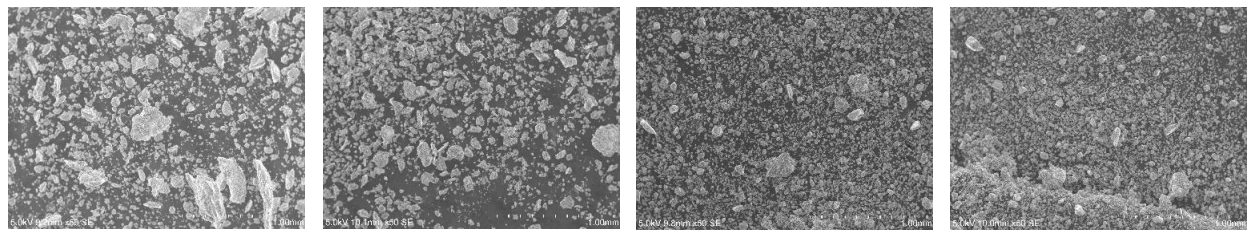


Fig. 4.14: SEM images comparing the Mg-NaCl mixtures with different weight% of NaCl milled for 1h, 3h, 7h, and 15h

4.4 EFFECT OF MILLING TIME AND WEIGHT PERCENTAGE OF KCl ON HYDROGEN GENERATION

The section highlights the effect of Mg-KCl on hydrogen generation in comparison with Mg-NaCl mixture for different milling time and weight percentage of salt.

Comparing the hydrogen generation between Mg 50%- NaCl 50% and Mg 50%- KCl 50% presented in Fig 4.15 show that greater amount of hydrogen is produced from Mg-KCl mixture relative to Mg-NaCl mixture. For the 15 h milled samples, Mg-KCl mixture generated approximately 200ml more hydrogen than Mg-NaCl for every 1g Mg used.

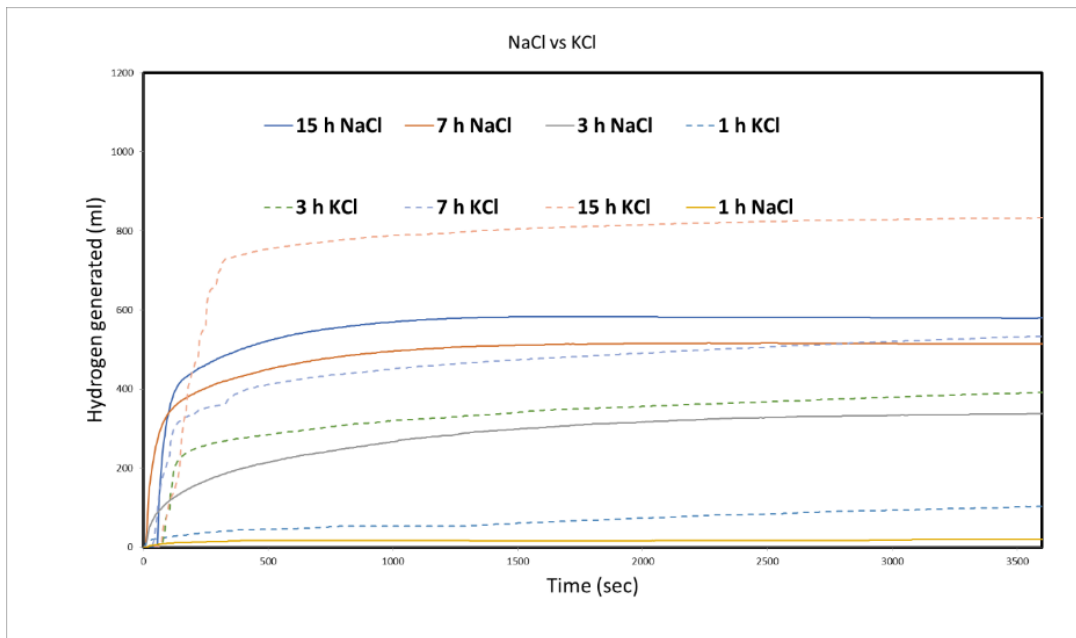


Fig. 4.15: Comparison of hydrogen generation between Mg 50%-NaCl 50% and Mg 50%-KCl 50% mixture ball-milled for 1 h, 3 h, 7 h, and 15 h.

This trend observed for hydrogen generation are similar to the previous results as discussed in section 4.2 and section 4.3. The increase in milling time improves hydrogen yield and increase in weight percentage of KCl in the mixture improves hydrogen yield.

Fig 4.16 shows the hydrogen generation for Mg-KCl mixtures with different wt% of KCl ball milled for 1h, 3h, 7h and 15h.

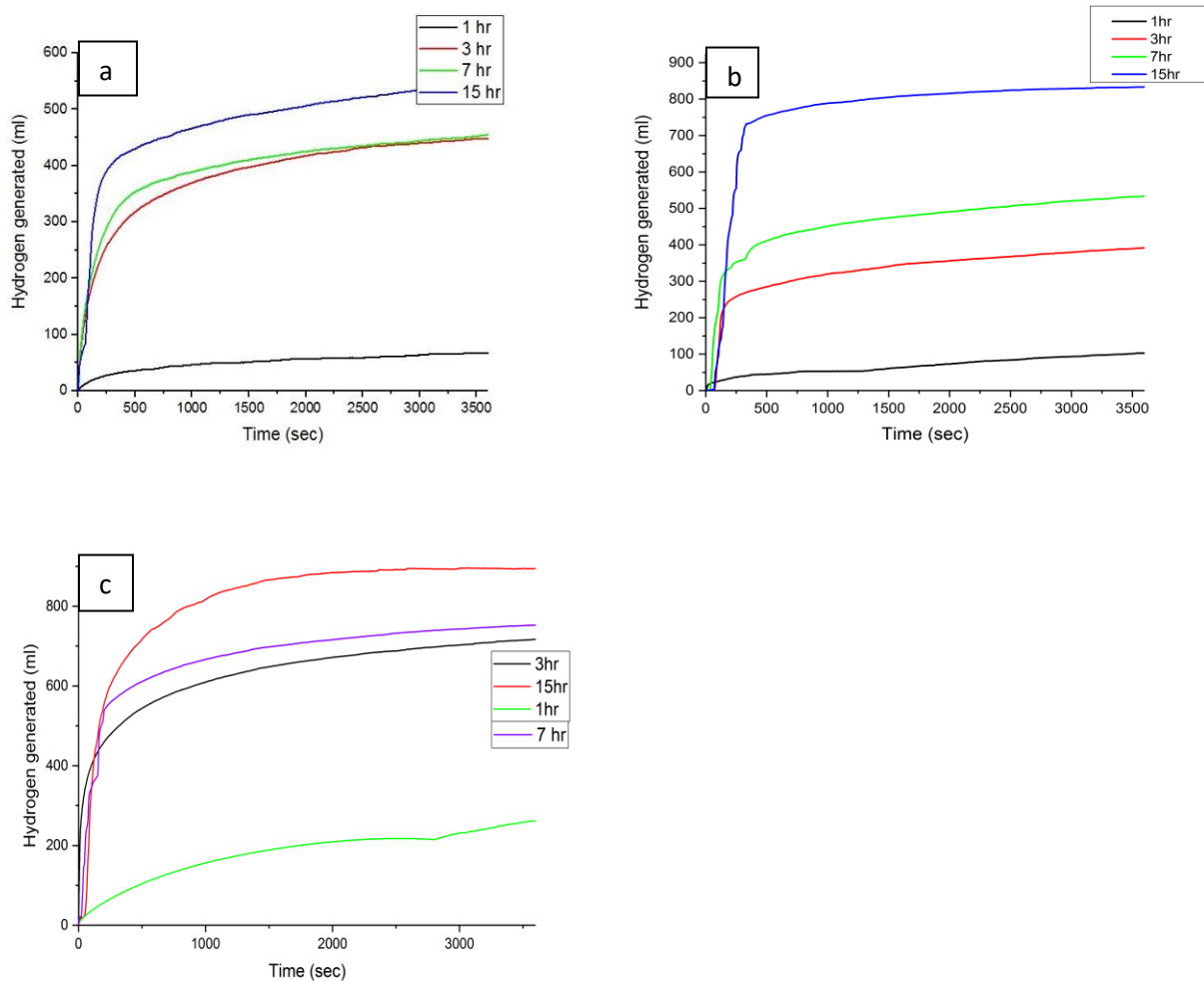


Fig. 4.16: Hydrogen generation profile for (a) Mg 75%-KCl 25% (b) Mg 50%-KCl 50% (c) Mg 25%-KCl 75% mixture ball-milled for 1 h, 3 h, 7 h, 15 h.

The maximum hydrogen yield of 895 ml for 1 g of Mg was obtained for Mg25%-KCl75% mixture ball milled for 15h.

These results are in agreement with the previous results of Mg-NaCl mixture as discussed in section 4.2 and 4.3. SEM and EDS results in Fig. 4.17 and 4.18 are also similar to the Mg-NaCl results which show higher refinement of particles with increased milling time and higher KCl wt%.

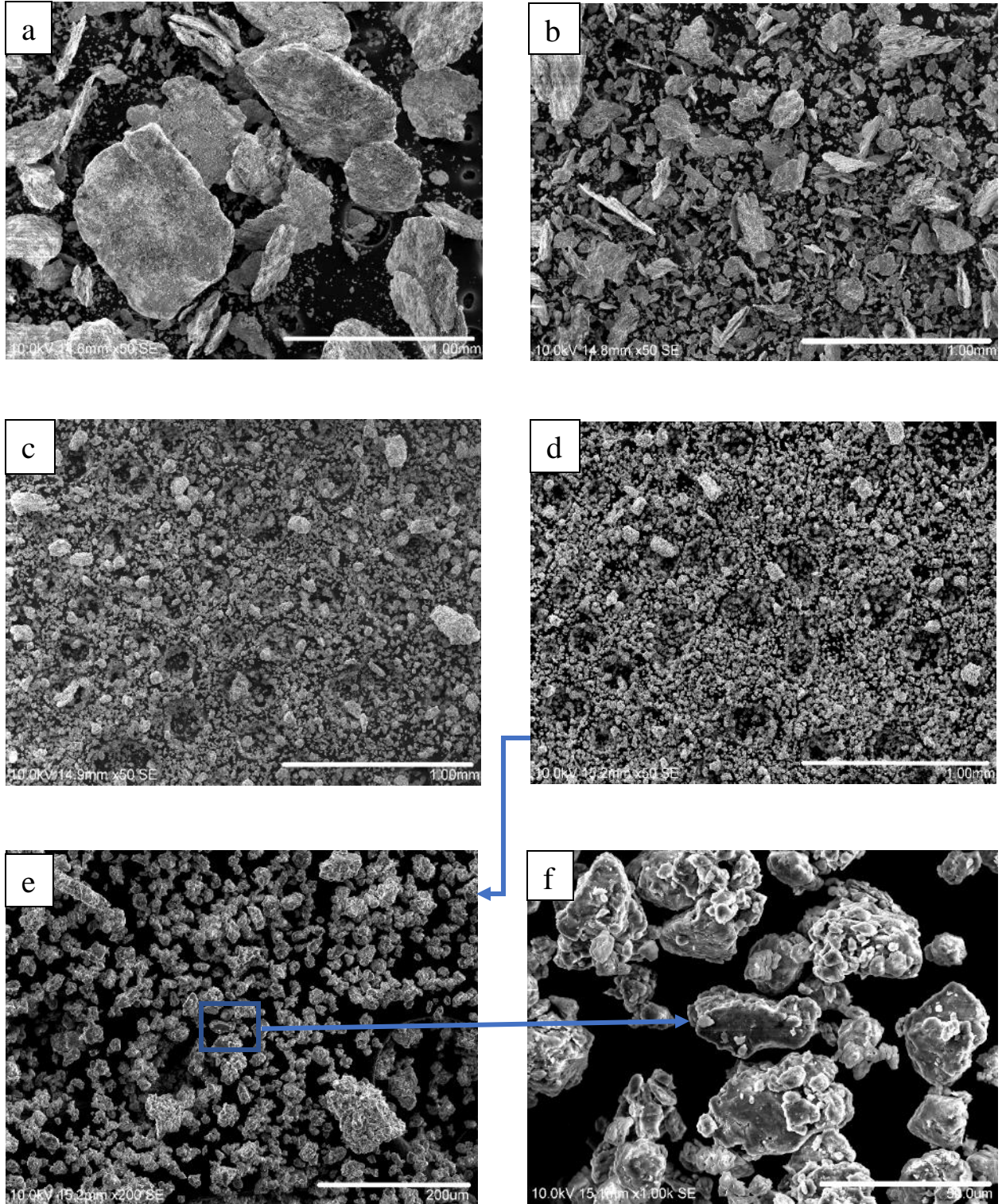


Fig. 4.17: shows Mg 75% and KCl 25% mixture ball milled for (a) 1 h (b) 3 h (c) 7 h (d) 15 h (e) enlarged image of (d) 200x and (f) Magnified image of (e) 1000x

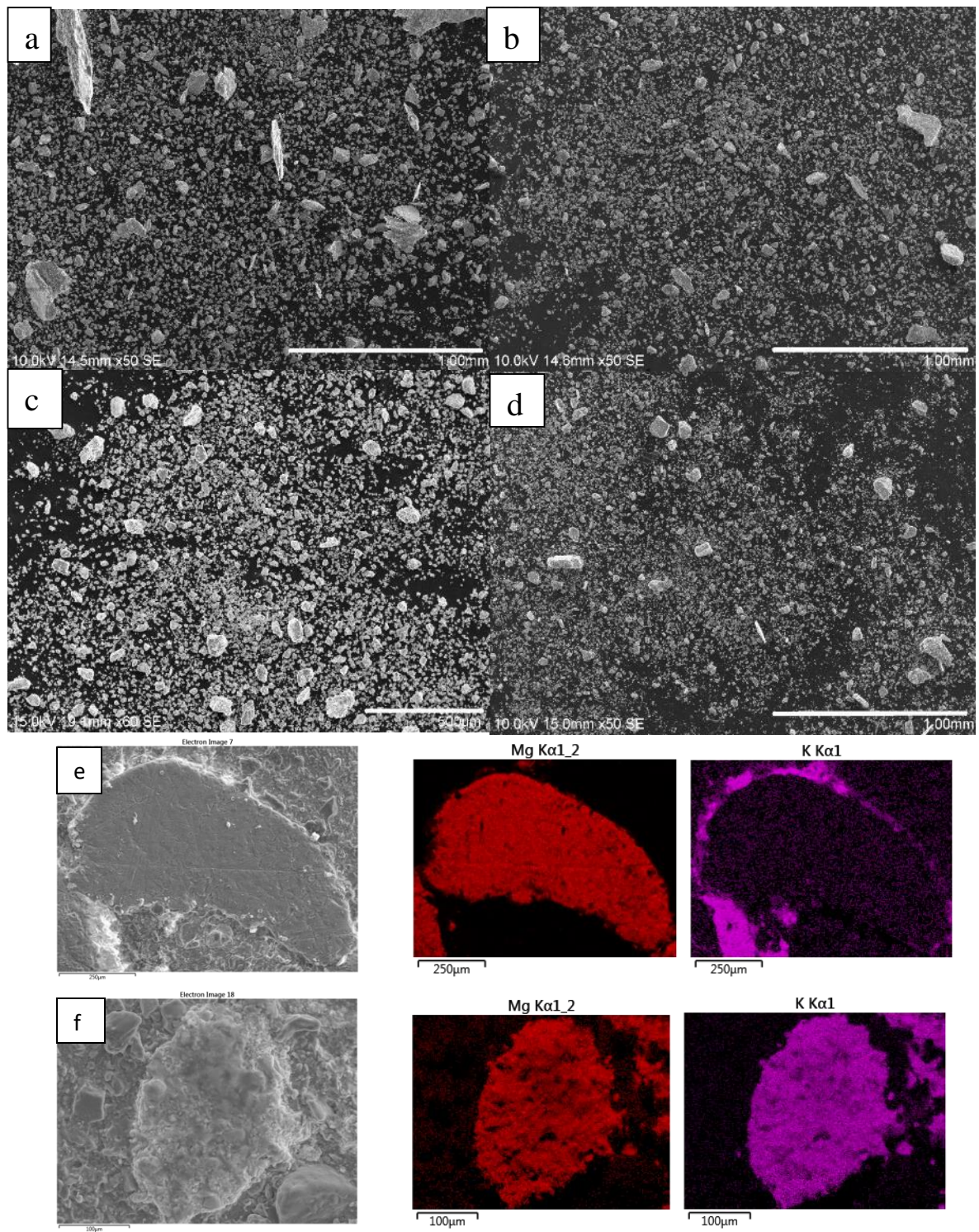


Fig. 4.18: Mg 25% and KCl 75% mixture ball milled for (a) 1 h (b) 3 h (c) 7 h (d) 15 h. EDS scans of the cross section of Mg-KCl mixture ball milled for (e) 1 h (f) 15 h

However, another trend is observed when comparing the hydrogen yields of Mg-NaCl and Mg-KCl. The hydrogen yield plots for 7 h and 15 h ball-milled mixture lies close to each other in Mg-NaCl mixture whereas for Mg-KCl mixture, the hydrogen yields for 3h and 7h ball milled mixture lie close to each other. It is for the same reason that Mg50%-KCl50% showed slightly better results when compared with NaCl. This might be attributed to higher hardness of KCl however more research needs to be done in this area (Razavi-Tousi & Szpunar, 2016).

4.5 ERROR ANALYSIS

To analyze the precision of the experiment, 3 tests were carried out under the same conditions. This allows us to ensure that the experiments conducted are reproducible. The error analysis is applied to the final hydrogen yield.

The reproducibility of the results for Mg50%-NaCl50% milled for 1 h is illustrated in fig 4.19.

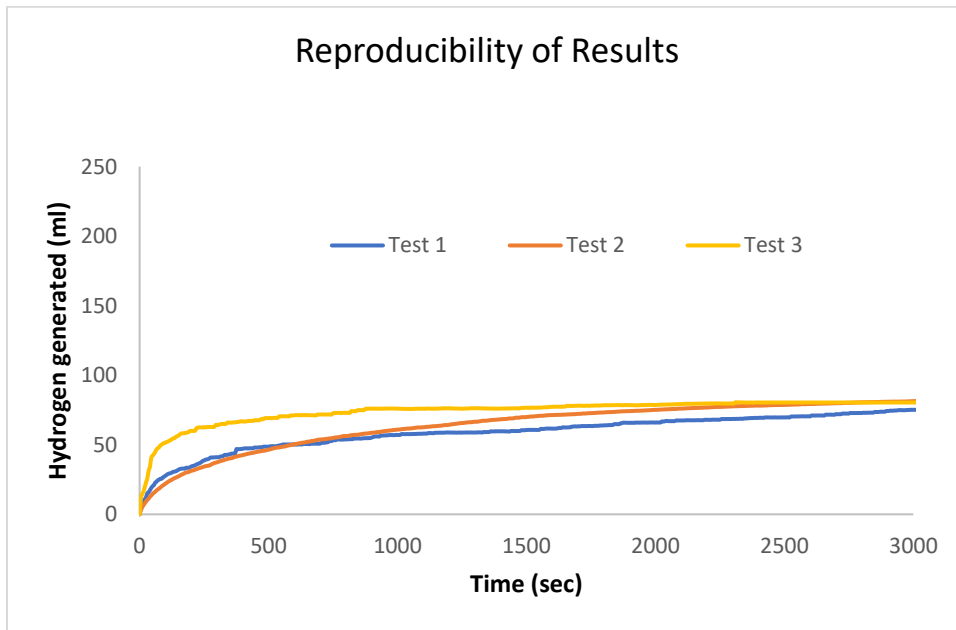


Fig 4.19: Reproducibility of result for Mg50%-NaCl50% milled for 1 hour

$$\text{Percent Difference} = \frac{|E1 - E2|}{\left(\frac{E1 + E2}{2}\right)} \quad 4.1$$

E1 and E2 represent the end point result (final hydrogen generation) of each pair of experiments.

The precision from the 3 different readings in Fig 4.19 measures the percentage difference in the final hydrogen yield of 0.7%- 7% which is 6 ml in variation. This variation in the final hydrogen yield can be applied to all other hydrogen generation experiments.

CHAPTER 5

CONCLUSION AND FUTURE WORKS

Judging from the experimental results, the following conclusions are drawn:

1. The steady-state time for milling (time after which further milling does not affect size and structure of the powder) of pure Mg powder was 15 h.
2. Hydrogen yield increased with milling time due to higher surface area for the reaction with water.
3. Hydrogen yield increased with concentration of NaCl within the Mg-NaCl matrix. KCl deployed as alternative process control agent exhibited better hydrogen generation rate.
4. SEM/EDS scans on Mg-NaCl particles reveal that higher milling time further refine uniformed Mg/NaCl distribution. This was also observed for Mg-KCl composite. The EDS maps of the cross section of these particles prove that the salt particles were embedded deep in the Mg matrix.
5. The highest yield was obtained for Mg-KCl 75% mixture ball milled for 15 h which resulted in 80% hydrogen generation in less than 10 min. The presence of salt (NaCl and KCl) enhanced the hydrogen generation rate as they prevented cold welding of Mg particles and favored brittle fracture. Also, the salt dissolved in water thus increasing the specific area which in turn increased the reaction rate. Both salts that were used are abundant, however there is still room for significant research on KCl composites to improve its performance.

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