

HYDROGEN GENERATION OF Al-NaCl POWDERS IN DIFFERENT REACTION MEDIUMS

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ABSTRACT

This work is a study of hydrogen generation of Al-NaCl powders in different reaction mediums. Water, KOH and NaOH were used as reaction mediums for the comparison of the hydrogen generation rate. The effects of the milling time, NaCl wt%, reaction temperature and reaction mediums were investigated. Al was milled with NaCl in order to increase the hydrogen generation rate. Increasing NaCl wt% and reaction temperature also increased the hydrogen generation rate. Al reactivity can be enhanced by increasing milling time, NaCl wt%, reaction temperature and by using alkaline solutions.

Key words: *Al-NaCl powders, ball milling, hydrogen generation, alkaline solutions.*

1. INTRODUCTION

Climate changes due to the emergence of CO₂ as a result of the use of fossil fuels have led to the search for alternative fuels. Bio-mass, wind, sun, hydrogen, nuclear etc. alternative energies can be given as examples (Ho, 2017). With its high chemical energy and environmentally friendly properties, hydrogen is one of the important new and clean energy sources (Yang et al., 2018).

Hydrogen can be produced by different methods, steam reforming, other production methods from fossil fuels (partial oxidation, plasma reforming etc.), from water (electrolysis, thermolysis, etc.), etc. (wikipedia, 2020). Hydrogen generation by Al water reaction is preferred because it reduces CO₂ production and has no harmful effects on the environment. Water is a cheap and clean source, Al is an abundant and economical metal. Al has high energy density of 29 MJ/kg, and theoretically it produces 1360 ml/g H₂. Al water reaction is given in equation (1). (Ho, 2017).



Reaction byproducts are non-corrosive, stable, and recyclable (Liu et al., 2012). Al can be remanufactured from Al(OH)₃ by-product (Liu et al., 2015; Ho, 2017; Dupiano et al., 2011).

Difficulties in Al water reaction are coating of Al metal surface with protective oxide layer and formation of dense hydroxide as by-product. To overcome these difficulties, various studies have been applied to activate aluminum and develop its hydrolysis properties (Liu et al., 2015). Addition of low melting point metals and forming alloys (Al–Ga, Al–Ga–In, Al–Li, Al–Mg–Fe, etc.) (Yang et al., 2018), use of water-soluble salts while reducing particle size with ball milling (e.g., NaCl, KCl, CoCl₂, NiCl₂, Na₂CO₃ etc.) (Yang et al., 2018; Rong et al., 2017; Czech and Troczynski, 2010; Razavi-Tousi and Szpunar, 2016; Yolcular and Karaoglu, 2017), use of alkaline solutions (NaOH, KOH, etc) (Pyun and Moon, 2000; Porciúncula et al., 2012). These methods are very effective in the removing of protective oxide layer on the Al particles and keeping the activation of Al powders.



Equation (1) gives the Al water reaction at low temperatures. The by product is Al(OH)₃ at low temperatures. Equation (2) gives the Al water reaction at high temperatures. At high temperatures the by product is Al₂O₃ (Rong et al., 2017).

When Al reacts with water firstly Al(OH)₃ forms. Then, it further reacts to form Al₂O₃. Al(OH)₃ and Al₂O₃ are amphoteric which means that they have both an acid and a base character. Al₂O₃ is not soluble in water. This prevents the Al corrosion in water. However, Al₂O₃ is soluble in alkaline solutions (Mcarthur and Spalding, 2004). Ball milling, increasing reaction temperature or use of alkaline solutions could be applied for the reaction to continue by dissolving the passive oxide films.

The equations of the reaction for NaOH to remove the passive oxide film from the Al particles with equations (3) and (4);



The reaction of NaOH with by products Al₂O₃ or Al(OH)₃ forms Al(OH)₄⁻. Al(OH)₄⁻ dissolves in NaOH solution and satisfies the continuation of the reaction by supplying fresh Al surfaces for the Al water reaction (Jia et al., 2014).

This study is about hydrogen generation of Al-NaCl powders in different reaction mediums. Pure water, NaOH and KOH were used as different reaction mediums in the hydrogen generation experiments. The parameters, reaction temperature, milling time and addition amount of NaCl were changed to investigate their effects in the hydrogen generation. This research examines how milling time, reaction temperature, addition of NaCl and reaction medium affect the Al water reaction.

2. MATERIAL AND METHODS

Al (average diameter 90 μm) and NaCl (Merck, 98%) were mixed and milled in a planetary ball mill (QM-3SP4) with a ball to powder ratio 20:1. NaCl wt% was 0, 10, 20 and 30 and 4, 8 and 16 h milling times were applied. Speed of the rotation was 200 rpm.

Hydrogen generation experiments were done in a 250 ml flask with two openings. When the reaction temperature was reached by placing the flask in the water bath, the ground powder was added to this flask. 35-75 $^{\circ}\text{C}$ reaction temperatures were investigated.

Pure water, NaOH (1 M) and KOH (1 M) were used as solution mediums to compare their effects at the hydrogen generation rate. Mixing applied during the reactions.

The hydrogen produced was measured at room temperature with an inverted burette filled with tap water. The amount of hydrogen production was recorded by monitoring the water level changes in the burette at certain intervals.

In our previous study (Yolcular and Karaoglu, 2017), reaction temperature was between 30 - 70 $^{\circ}\text{C}$, NaCl amount was 0, 5, 10 and 20 wt%, milling times were 1, 4 and 12 h. According to our results in our previous study we determined these different temperature, grinding time and NaCl amounts in order to investigate their effects in this study. Unlike our previous study, experiments were carried out in different reaction mediums. The effects of different reaction mediums were investigated with selected reaction temperature, grinding time and NaCl amounts.

3. RESULTS AND DISCUSSION

Ball milling was applied to Al powders in order to increase the surface area by decreasing the particle size. This could be reached with the addition of NaCl during the ball milling. The addition of NaCl prevented cold welding during milling and assisted in the crushing and grinding of the particles. Pure Al and increasing wt% of NaCl additions were investigated in hydrogen production experiments. Figure 1 shows the effect of the amount of NaCl added by the addition of 10, 20 and 30 wt% NaCl. These added NaCl amounts also compared to pure Al powders. As the amount of NaCl increased the particle size decreased and surface area of the particles increased. This Al - water reaction is a surface reaction and the reaction rate is relevant to total surface area of the powders. (Nie et al., 2012) (Bunker and Smith, 2011). The addition of NaCl and milling is effective, but they cannot show the same effect when each is applied individually. So, there is a strong synergy between the grinding process and the presence of a salt (Razavi-Tousi and Szpunar, 2016). From Figure 1, 30 wt% NaCl addition gives the highest hydrogen generation rate.

Figure 1. Hydrogen generation (HG) rate ($\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) vs time (min) with different wt% NaCl additions, in 1 M NaOH solution, with 16 h milling and at 75 °C.

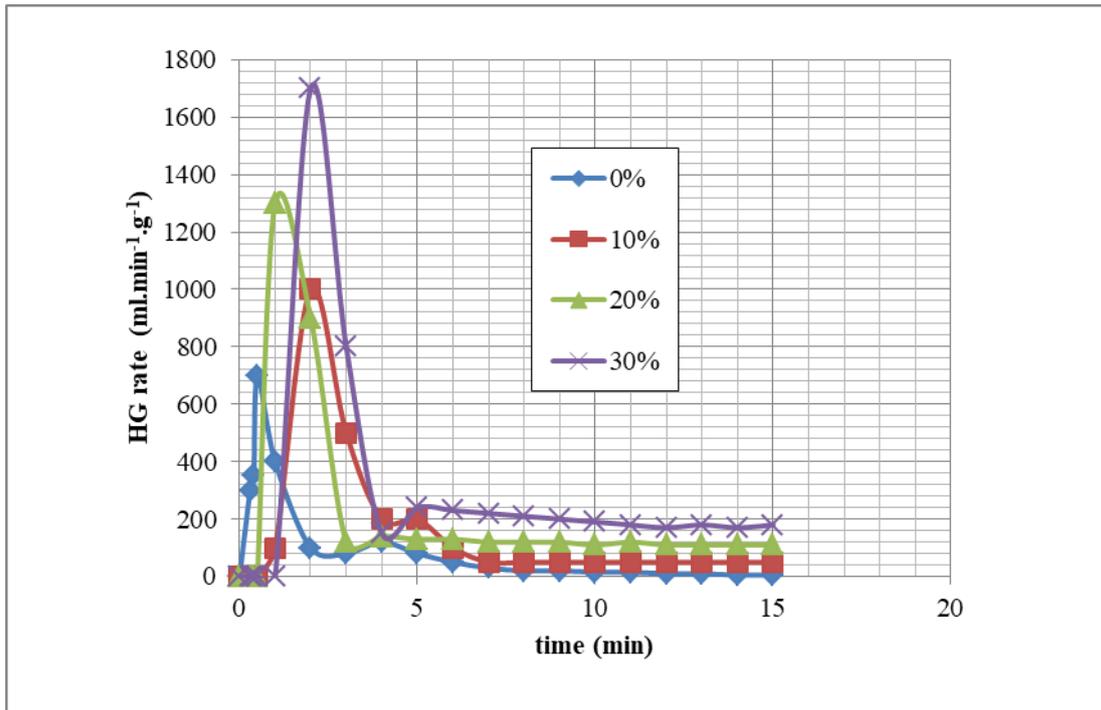


Figure 2 gives the results of increasing milling time. Ball grinding activates the particles so that they can react easily. Hydrogen generation rate increases with increasing milling time. Particle sizes decreased with increasing grinding times, which allowed the particles to have larger surface area. In this study, 16 h milling gave the highest hydrogen generation rate. The milling changes nonporous structure of the particles to porous structure having high surface area. These pores provide a higher surface to the reaction.

Figure 2. HG rate ($\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) vs time (min) with different milling times, with 30 wt% NaCl addition, in 1 M NaOH solution and at 75 °C.

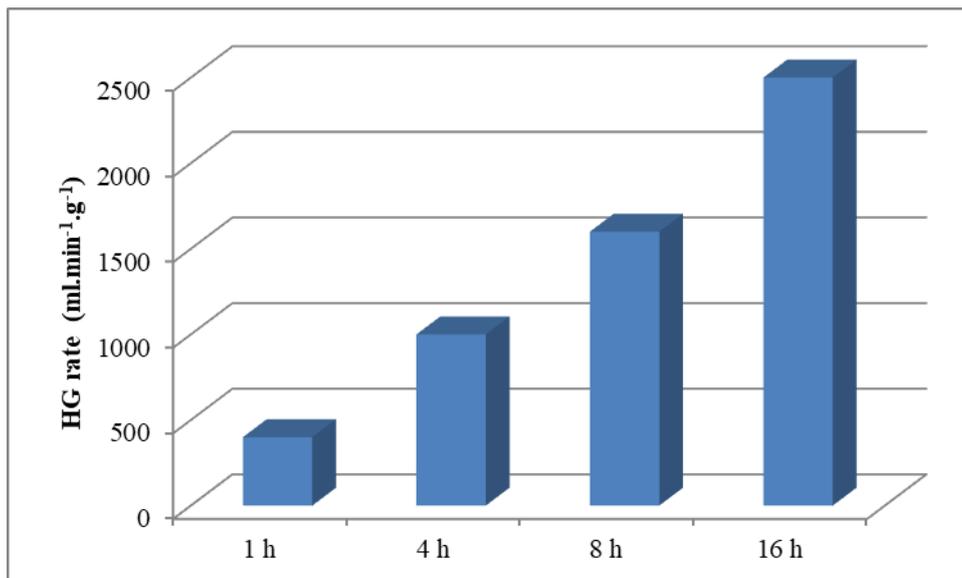


Figure 3 shows the effect of temperature on hydrogen generation with 16 h milling, 30 wt% NaCl addition to Al powders. 35 – 75 °C reaction temperatures were investigated for these samples. The increased reaction temperature was resulted in higher reaction rates. As 75 °C gives the highest reaction rate, this temperature was used in other experiments. During the reaction the passive oxide film which was formed on the surface of Al powders can be quite permeable at higher temperatures compared to low temperatures. Then the reaction continues for a long time and higher reaction rates also can be reached.

Figure 3. HG rate ($\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) vs time (min) with different temperatures, with 30 wt% NaCl addition, in 1M NaOH solution and at 16 h milling time.

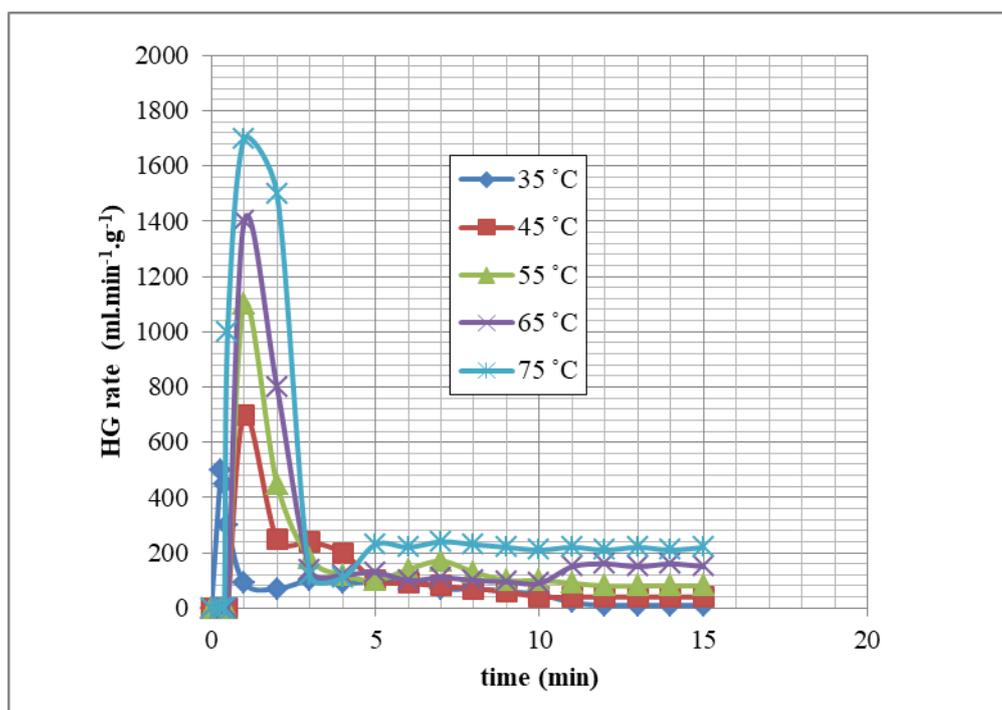
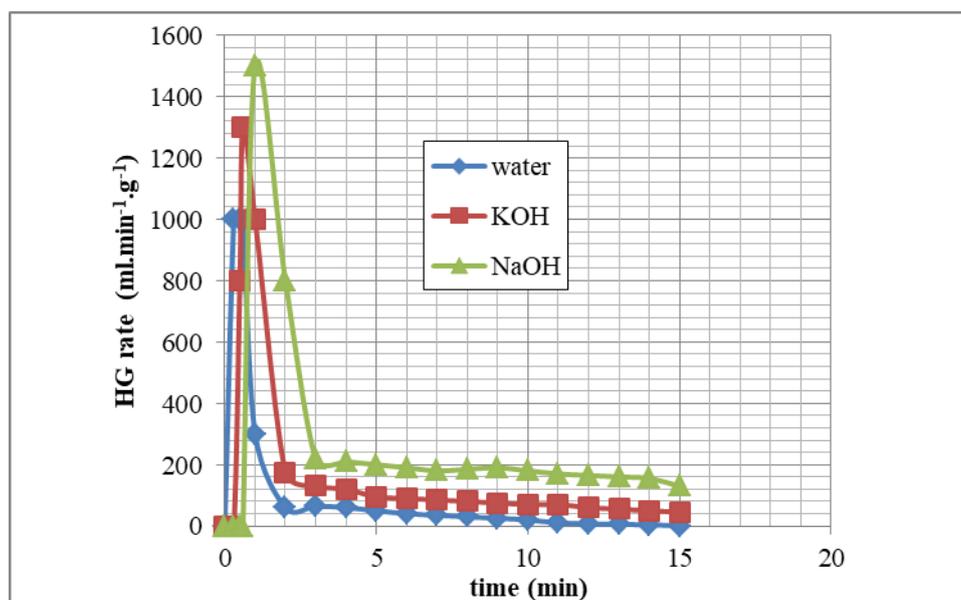


Figure 4 shows that higher reaction rates were achieved with NaOH solution when comparing water, NaOH and KOH solutions. Reaction mechanisms were different for each reaction medium. Activation energies vary according to the reaction medium. Reaction activation energy is higher with water and KOH solution and lower with NaOH solution. This results in higher hydrogen generation rates due to the low activation energy of experiments with NaOH solution. The activation energies were found for this study as; 53.2 $\text{kJ}\cdot\text{mol}^{-1}$ with water, 49.4 $\text{kJ}\cdot\text{mol}^{-1}$ with KOH (1 M) solution and 45.7 $\text{kJ}\cdot\text{mol}^{-1}$ with NaOH (1M) solution by using 30 wt% Al-NaCl powder. According to these results, highest hydrogen generation rate was observed with NaOH solution.

Figure 4. HG rate ($\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) vs time (min) with water, NaOH and KOH solutions, at 75 °C, with 30 wt% NaCl addition and at 16 h milling time.



4. CONCLUSIONS

The addition of NaCl to Al powder affects the hydrogen generation reaction. The structure of the Al particles also affected by both NaCl addition and ball milling. Hydrogen generation rate and produced hydrogen amounts were increased by NaCl addition and ball milling. The salt mixed while grinding is dissolved in water or aqueous solution during the reaction, creating many cavities, voids, tunnels in aluminum particles to make the reaction happen and improves the kinetics of the reaction. The addition of a higher salt ratio allows the particles to have a higher surface area, which increases the reaction kinetics. Then, containing a higher percentage of weight Al powders showed higher hydrogen generation rates. Mixing the reaction solution during the reaction and using higher reaction temperatures prevents the formation of passive oxide film and ensures that the formed film is also permeable. Reaction activation energies change by different reaction mediums. In this study, water, KOH and NaOH solutions were compared and their activation energies also calculated as; $53.2 \text{ kJ}\cdot\text{mol}^{-1}$ with water, $49.4 \text{ kJ}\cdot\text{mol}^{-1}$ with KOH (1 M) solution and $45.7 \text{ kJ}\cdot\text{mol}^{-1}$ with NaOH (1M) solution by using 30 wt% Al-NaCl powder. The results showed that experiments with NaOH solutions has lower activation energies which means that the corrosion reaction continues easily without disruption because of passive oxide film. Highest hydrogen generation rate was observed with NaOH solution as $1500 \text{ ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. Similar studies on activation energy data are as follows: $46\text{-}53 \text{ kJ}\cdot\text{mol}^{-1}$ with NaOH (between $20\text{-}70 \text{ }^\circ\text{C}$) (Zhuk et al., 2006) $51.5\text{-}53.5 \text{ kJ}\cdot\text{mol}^{-1}$ with $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH (Aleksandrov et al., 2003) $69 \text{ kJ}\cdot\text{mol}^{-1}$ with addition of lithium as promoting metal without any alkaline solution (Rosenband and Gany, 2010). The activation energy ranges between approximately $40\text{-}70 \text{ kJ}\cdot\text{mol}^{-1}$ and changes according to reaction medium, reaction temperature and Al particle properties. Increasing milling time, NaCl wt%, reaction temperature and by using alkaline solutions enhances Al reactivity. Al can be used effectively to generate hydrogen by Al water reaction.

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