EFFECT OF ALKALINE CONCENTRATION ON THE HYDROGEN GENERATION

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ABSTRACT

Aluminum (Al) and water reaction is one of the preferred hydrogen production methods. However, the protective layer of oxide which forms and covers the surface which prevents or delays the reaction during this reaction is a problem. In this study, in order to overcome this problem ball milling was applied and NaOH solutions with different concentrations were used in the reactions. Al powders were grounded with NaCl and 0.5, 1, 1.5, 2 M NaOH solutions were used. Influence of alkaline concentration was researched on the experiments. Results showed that, higher temperatures and increased concentrations of NaOH solutions improves the hydrogen generation rate.

Keywords: Hydrogen generation, Al powder, Al water reaction, ball milling, NaOH concentration

1. INTRODUCTION

In recent years, many studies are carried out to discover a regenerative and pure energy source to satisfy the needs. Hydrogen emerges as a promising alternative energy source. Among many hydrogen production methods, Al and water reaction is also very important. Aluminum is plentiful and low-cost material. It has high theoretical hydrogen capacity and 1 mol of Al gives 1.5 mole H_2 [1 - 3]. Al has higher density of energy and it has high standard potential -1.67 V. Al is a perfect reducing agent with this high negative standard redox potential. Because of this property Al can give reaction easily and produces H_2 [4].

Reaction was given with equation (1).

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2\, H_2 \qquad (1)$$

By-products formed by Al water reaction, Al_2O_3 and Al $(OH)_3$ can be easily recycled. For all these reasons, Al and water reaction is preferred in hydrogen production. However, passive oxide film formed on Al surface in aqueous solutions close to pH 7 prevents Al from reacting with water. Since this film is amphoteric, it can dissolve in strong, acid and base solutions. Then, either of the acid and base Al reaction can be applied to this production. Because of environmental conditions strong acid and base solutions were not preferred. Then, near neutral conditions preferred and other alternative methods investigated to remove this passive oxide film [4].

When this film region formed, reaction is constantly interrupted. Essential factor in rapid and effective generation is removal of formed passivation layer [1]. Different studies are carried out to destroy this passive oxide film. The use of NaOH, KOH, $NaAlO_2$ and $Ca(OH)_2$ solutions is one of them [1, 5 - 8]. The other studies, alloys prepared with the addition of metals (Al-Li, Al-Ga, Al-Mg-Fe, Al-Ga-In, Al-In-Ga-Sn etc.) [9 - 11]. Others are, ball milling with water soluble salts (KCl, NaCl, $CoCl_2$, Na_2CO_3, $NiCl_2$ etc.) [2, 12 – 14]. The other ones are, oxide additives (Al_2O_3,Co_3O_4, CaO, etc.) by ball-milling [15 – 17].

The use of water soluble salts in the milling as milling asistant agent accelerates the hydrogen generation rates by the formation of micro galvanic cells [18]. NaCl which was added during the milling can be distributed on the Al surface, in the cracks, voids and tunnels. Then agglomeration and cold welding was inhibited along ball grinding [1]. The addition of NaCl provides free Na^+ ion, this ion combines with the OH^- ion and this combination increases the pH of the solution. This produced NaOH acts as a catalyst for hydrogen production and ensures the continuation of hydrolysis [19].

NaOH removes passive oxide film, equation (2), (3) and (5) shows the use of NaOH solution [5, 14].

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2 \quad (2)$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \quad (3)$$

$$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3 \quad (4)$$

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^- \quad (5)$$

NaOH was consumed to produce hydrogen as shown by equation (2). Equation (3) shows the decomposition of the $NaAl(OH)_4$ and regeneration of NaOH. In the equation (4) Al_2O_3 forms $Al(OH)_3$. [14]. The passive layer formation on surface and removal of this layer by $(OH)^-$ affects the hydrogen generation rates [5].

NaOH behaves like a catalyzer in this hydrolysis reaction. Equation (3) shows that, $NaAl(OH)_4$ decomposes and regenerates NaOH and $Al(OH)_3$. This causes to increase in the NaOH concentration. Then, hydrogen generation rate and hydrogen production amounts increase by this higher NaOH concentrations [19].

The resulting hydrogen generation reaction by-product aluminum hydroxide able to inhibit inactivation. Presence of aluminum hydroxide activates Al corrosion reaction to produce H_2. Equation (5) shows use of NaOH and by-product aluminum hydroxide which forms $Al(OH)_4^-$. Dissolution of $Al(OH)_4^-$ by NaOH provides continuity of the reaction by removing passive oxide film from the Al surface to expose clean reactive surfaces for the reaction [6].

$Al(OH)_3$ could be employed as an activator for this hydrolysis reaction. The by-product aluminum hydroxide could be used for aluminum generation either could be employed for any other purposes, e.g. for water treatment or as flame retardant [5].

Increasing the reaction temperature and alkaline concentration at the same time creates a synergistic effect [20].

However, higher concentrations of alkaline solutions were not preferred because of environmental reasons, there was a need to use sometimes with small amounts of increase or higher in the alkaline concentrations to improve hydrolysis reaction. Then, by this study effect of alkaline concentration was studied with the effect of temperature. Influence of alkaline concentration was researched for removal of passive oxide film. Additionally, influence of reaction temperature on hydrogen generation was researched. Added NaCl amount, milling time values were kept constant for the comparison of NaOH concentration.

2. EXPERIMENTAL

In the experiments, NaOH concentrations were 0.5, 1, 1.5, 2 M for the comparison of their effects at the hydrogen generation rate. Al with an average diameter 90 µm and NaCl (98%) was supplied by Merck were mixed and grinded. 20wt% NaCl was used and 12 h milling time were applied. Speed of the rotation was 200 rpm.

Hydrogen generation experiments were done in a two neck glass which has two exits at 35 - 75 ˚C. Experimental set-up was given at the Figure 1. When steady - state conditions were reached with placing this glass in the heater, ground powder was added to this flask. The hydrogen generation was started when the powder was added to the alkaline solution.

The hydrogen produced was measured with a silicon tube by the connection of erlenmeyer and inverse burette. The level changes in this burette were used to measure the production amount. The given reaction conditions were applied to investigate the effect of NaOH solution concentration.

Figure 1. The Experimental set-up.

3. RESULTS AND DISCUSSION

For this reaction increase of aluminum amount causes an increase in production rate. At beginning of reactions production rate is higher; as reaction proceeds the formed passive oxide film inhibits the corrosion reaction. Then after a passivation period, reactivation was achieved. These passivation reactivation periods continue during the reaction and according to reaction conditions. This procedure links to aluminum hydroxide film formed above surfaces to produce H_2. This thin layer continues to react with Al and captures the water molecules [5, 16]. This produced H_2 remains beneath this oxide film up to the compression of H_2 breaks this oxide layer by micro explosion [5]. Then Al could react with water or aqueous solutions. Continued hydrogen generation could affect the other passivated Al particles to reactivate by the help of increased temperature and micro explosions. The reactivation times were different according to used amount of Al and reaction conditions. According to control reactivation, some alternative methods can be used. In this study, the reactivation of Al particles supplied by grinding of aluminum powders adding 20 wt% NaCl and using NaOH solutions. NaOH solutions with 0.5, 1, 1.5, 2 M were used for continuous reactivation of Al powders. 12 h ball milling was applied to Al powders.

The addition of NaCl to Al powder during ball milling also help to remove the passive oxide film. NaCl particle size also decreases by this process. Then the surface area of Al particles increases which satisfies the higher hydrogen generation rates. During ball milling, many indentations, ridges, pores and tunnels was formed on Al particles. All of these increases the surface area of Al particles which provides many spaces for the reaction to take place. NaCl, which is placed in Al powder with ball milling, dissolves easily with water during the reaction and reveals more clean and reactive surfaces on the Al. The hydrogen generation rate increases by this way.

Occasionally, the reaction was stopped and interrupted due to passivating aluminum hydroxide layer formed. Performed passive oxide films can be dissolved in the NaOH solutions. The use of NaOH solution improves the reaction conditions. Al and water reaction passivation can be dealed by using alkaline solutions. NaOH acts as a catalyst and removes the performed passive oxide film. During the reaction by the dissolution step of $NaAl(OH)_4$ the produced NaOH increases the pH of the solution. Increasing pH helps removing the protective oxide film. Hydrogen generation rate values show the influence of the alkaline effect. Figure 2 illustrates this influence in hydrogen generation. As NaOH solution concentration increased between 0 – 2 M of NaOH concentration, production rate also improved. In this study, highest concentration was 2 M for NaOH and it gave the highest reaction rate.

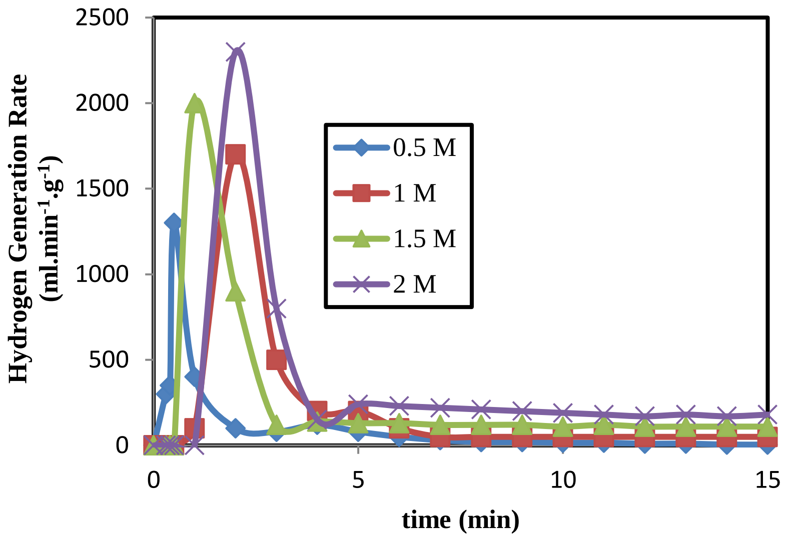

Figure 2. Hydrogen generation (HG) rate vs. NaOH concentration with 75 ˚C, 20 wt% NaCl addition, 12 h milling.

Figure 3 represents influence of temperature for production rate. This reaction is temperature sensitive. When the reaction temperature was raised reaction is very fast. The higher reaction temperatures give higher hydrogen generation rates. Production rate was 2300 $ml.min^{-1}.g^{-1}$ at 75 ˚C. At higher temperatures diffusion also increases and this improves the reaction kinetics. The permeability of the passive oxide films change with the temperature. Higher temperatures increase the permeability of the passive oxide film. The hydrogen generation rate at 75 ˚C was higher with these advancements.

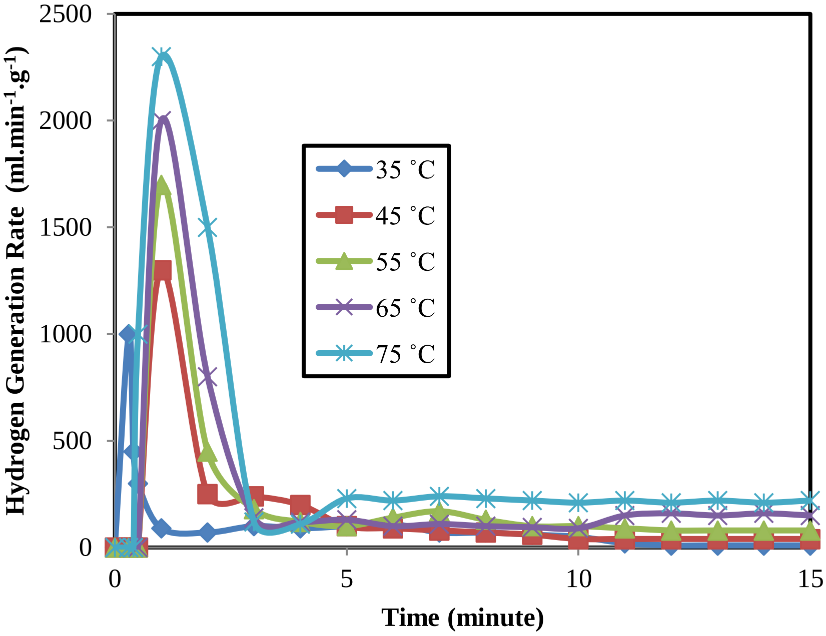

Figure 3. HG rate vs. reaction temperatures, 20 wt% NaCl, 2 M NaOH, and 12 h milling.

Figure 4 shows the highest hydrogen generation rates by these reaction temperatures in this study. As can be seen in this figure that there is a tendency to rise in the rate by the increasing temperatures.

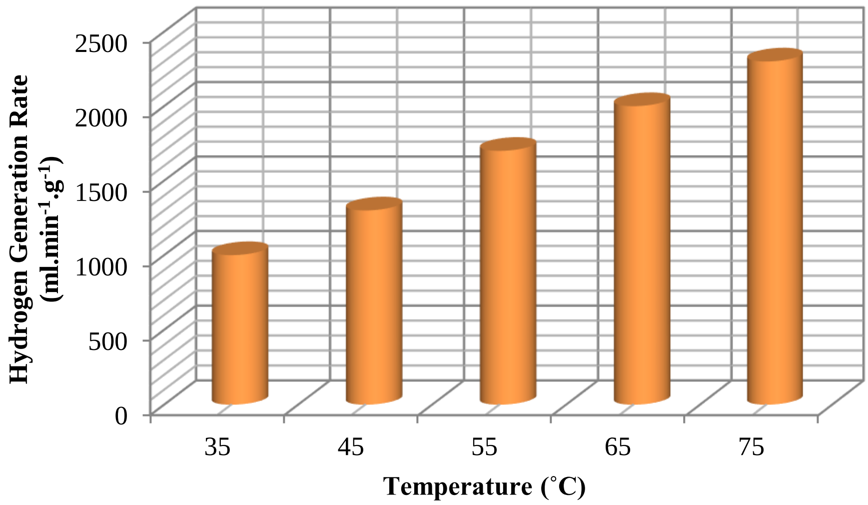

Figure 4. Highest HG rates vs. reaction temperatures, 20 wt% NaCl, 2 M NaOH, and 12 h milling.

Advanced hydrolysis rates were gained with the increase in NaOH concentration. Likewise by raising temperature higher reaction rates were achieved. There is a mutual interaction between temperature and concentration increase.

3. CONCLUSIONS

Experiments have been conducted to find the effects of temperature and alkaline concentration, which are crucial points to increase the hydrolysis rate. There is simultaneous interaction between temperature and concentration increase. Hydrogen generation rate is controllable with the variables, temperature and NaOH concentration. Increasing NaOH concentration leads to a rise in corrosivity, resulting in rise in hydrolysis rate. The hydrogen production increases with high temperatures. Added NaCl amount and milling times also effective on the hydrogen generation rates. NaCl particles were placed inside aluminum particles during ball milling. These salt particles dissolves in water or alkaline solutions by creating numerous fresh and reactive spaces and reaction areas on Al surfaces. Hydrogen generation rate was improved by higher alkaline concentrations. Influence of alkaline concentrations for Al and water hydrolysis indicates that increase in the concentration gives higher hydrogen generation rates. Although high concentrations are not preferred for environmental reasons, the hydrolysis controllable with slightly increasing concentrations if necessary. By increase in the alkaline concentration passive oxide film can be removed easily and this removal increases the reaction rate. Hydrogen generation rate was the highest using 2 M NaOH at 75 ˚C, 20 wt% NaCl addition and 12 h milling. The investigations show that this reaction is preferred in the generation of hydrogen. Pure hydrogen can be produced by this clean, safe and environmental friendly method.

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