

Hydrogen Generation From Aluminum In A Non-Consumable Potassium Hydroxide Solution

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ABSTRACT

A method to produce high purity hydrogen using reactions of aluminum with potassium hydroxide solution is studied. Theoretically, this process only consumes water and aluminum. There is no consumption of potassium hydroxide because the potassium aluminate produced in the hydrogen generation undergoes a decomposition reaction that regenerates the alkali. However, a small part of potassium hydroxide was lost during the process, diminishing the reaction rate, because CO₂ reaction with alkaline solutions in contact with air. Since aluminum corrosion is an exothermic process, it generates hydrogen and the heat necessary to carry out the reaction at optimal temperature (70-80°C) for an acceptable rate. Therefore, this process could be competitive for in situ production of hydrogen.

Keywords: Hydrogen production, alternative technologies, aluminum, caustic corrosion

1. INTRODUCTION

Nowadays, large amounts of hydrogen are consumed in several industrial processes like production of bulk ammonia and methanol, gasoline refining and hydrogenation of fats and oils. Moreover, the hydrogen requirements are rising because of the growth of its application in pharmaceuticals, metallurgy, semiconductor and aerospace industries, among others. It is expected that the market growth for fuel cells will increase the demand even further. [Hoffmann P. (2002)]

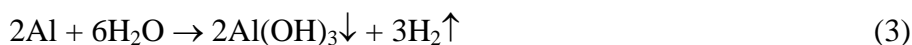
Likewise hydrogen is an attractive fuel alternative for the future, an attractive method for hydrogen production must be employed in order to maintain its positive profile. Other challenges that must also be addressed include the methods of hydrogen storage and transportation.

Generation of hydrogen for fuel cells by reaction of hydrides with water or aqueous solutions reduces storage weight and/or volume over high pressure or cryogenic storage [Belitskus (1970)], but this procedure is expensive. For instance, the price of sodium borohydride was approximately 20-25\$/lb [Chemical market reporter (2000)], which is too high to be applied for general hydrogen production. Contrary, the corrosion of aluminum in aqueous alkaline solutions provides a compact source of hydrogen that is relatively inexpensive considering the comparative price of aluminum powder, approximately about 4\$/lb. In this way, aluminum can be considered as a hydrogen storage material, since it behaves like a chemical hydride in contact with alkaline water.

The hydrogen generation reactions can be achieved under mild conditions of temperature and pressure, making this process attractive to produce hydrogen as a fuel. The potential applications of this technology include a system for a mobile fuel source for a H₂/air fuel cell, which could be competitive with the hydrogen sources conventionally used in conjunction with fuel cells such as methanol reformers and hydride storage beds.

The reaction of aluminum with sodium hydroxide solution to produce hydrogen has been already studied [Belitskus (1970), Stockburger et al (1992), Andersen and Andersen (2003)]:



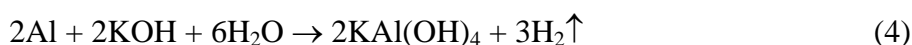


where (3) is the global reaction of steps (1) and (2). So, sodium hydroxide consumed in the hydrogen-generating reaction (1) can be regenerated in reaction (2). The relative rates of reactions (1) and (2) will affect both the rate and the extent of hydrogen evolution if a stoichiometric amount of sodium hydroxide is not present [Belitskus (1970)].

The major impediment to the production of hydrogen via this corrosion reaction is that the aluminum surface is easily passivated [Stockburger et al (1992)]. Nonetheless, surface passivation can be minimized optimizing several experimental parameters such as temperature, alkali concentration and aluminum scrap material. The optimum temperature was defined as the temperature at which the highest rate of hydrogen production was realized and at which the reaction was still controllable, and it was determined to be 70-90°C. The optimum alkaline concentration was defined as the alkaline concentration that minimized the mass of NaOH and H₂O required for the generation of hydrogen, since minimization of the mass of these reactants plays an important role in maintaining a high hydrogen mass storage fraction in the system. This concentration was determined to be 5.75M NaOH.

For all the experiments in Stockburger et al (1992), no Al(OH)₃ precipitation was observed when freshly made NaOH was used. The general hydrogen production trend observed was that a maximum hydrogen production rate was attained after a short induction period, after which a decrease was observed. This decrease was attributed to the increasing saturation of the NaOH with aluminum resulting in aluminum passivation. On the other hand, precipitation was observed when a pre-saturated alkaline solution was used. In the precipitating system, the rate of reaction of the aluminum slowed to unacceptably low levels as the solids content of alkaline solution approached 50% by weight. The development of two hydrogen generators with different rates: (5Lpm and 50Lpm) was also described. Those systems operated successfully concerning hydrogen generation rates, but they needed some improvements such as aluminum feed system, system pressure control or waste heat removal.

On the other hand, the behavior of KOH as the reacting base has been scarcely studied so far. Therefore, the objective of this work is to demonstrate the feasibility of KOH as alkali compound for producing hydrogen from aluminum. This research is focused in the study of the following reactions:



Namely, the hydrogen production step and alkali regeneration step, respectively.

2. EXPERIMENTAL

Potassium hydroxide 85% was supplied by Panreac. Aluminum foil was supplied by Albal. Hydrochloric acid was supplied by JT Baker. Tris(hydroxymethyl)-aminomethane was supplied by Merck. Tap water (not deionized) was used in all hydrogen generation runs unless otherwise noted.

Hydrogen generation was carried out in a Pyrex Erlenmeyer, which capacity was 500 ml, containing 200 ml of a potassium hydroxide aqueous solution from 0.1M to 5M. Aluminum foil was cut into little pieces. Each piece of aluminum foil was crumpled until forming a small ball, with a weight about 0.05-0.1g. In preliminary experiments 0.1g Al was added into the alkaline solution and aluminum consumption time was measured. In long term experiment, aluminum was added into the alkaline solution in small amounts, trying to keep a temperature between 70°-80°C.

When a large amount of precipitate was observed at the bottom of the Erlenmeyer, aluminum addition was stopped and reactive alkaline solution was filtered using a vacuum pump and a funnel provided with a filter plate. Precipitate was dried in an oven at 75°C during 3 days and was weighted. Each fraction of precipitate filtered was analyzed using X-ray diffraction and Attenuated Total Reflectance-Fourier Transform Infra Red (ATR-FTIR) spectroscopy in order to determine its composition. Filtrate solution was transferred into a 200 ml flask, adding tap water to complete 200 ml and a sample of the resultant solution was titrated with HCl 0.1547M (standardized using Tris(hydroxymethyl)-aminomethane) in order to determine total alkali concentration, using methyl orange as indicator of end point. Alkali solution was used again to hydrogen generation up to five more times.

3. RESULTS AND DISCUSSION

Aluminum pieces in potassium hydroxide solution produce hydrogen following reaction (4). Aluminum corrosion generates hydrogen and heat, with only tap water consumption (reaction 3). In the following sections the results obtained on the effects of several parameters and the results obtained for a long term experiment are reported.

3.1 Influence of temperature

Several experiments were carried out in order to study the temperature effect in hydrogen production. Experimental results using 0.1g Al and KOH 1M are reported in Figure 1:

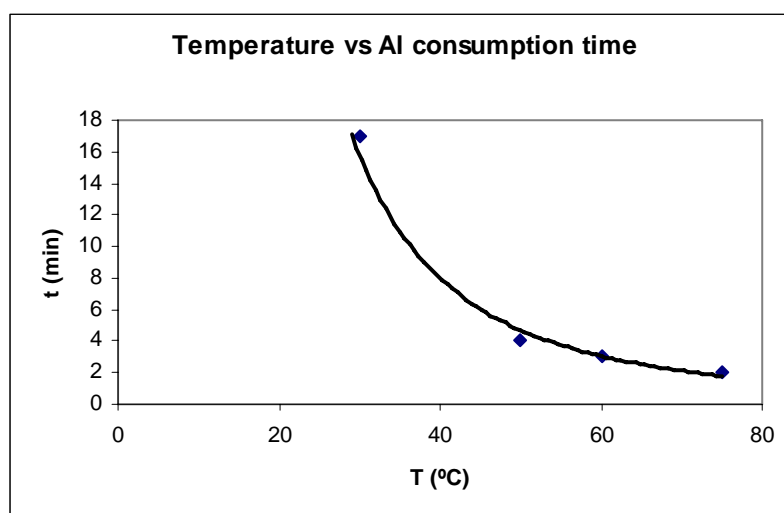


Figure 1: Influence of temperature on aluminum consumption time in hydrogen generation.

So, Aluminum consumption was faster when the working temperature was higher. This supplementary energy input to the alkaline solution allowed to get lower consumption times at constant KOH concentration and, consequently, higher hydrogen production during the experiments. Note that hydrogen production provides the heat necessary to carry out reaction (3) at optimal temperature with an acceptable rate, since about 130 ml of hydrogen can be theoretically achieved by consumption of 0.1g of aluminum. Therefore, there is no need to warm up the alkaline solution externally, because this is an exothermic process.

3.2 Influence of alkali concentration

Some experiments were carried out with the aim of study the alkali concentration effect in hydrogen production. Experimental results using 0.1g Al at different temperatures and different KOH concentrations are reported in Table 1:

Temperature (°C)	[KOH] (M)	Al consumption time (min)
25	5	3
	1	18
	0.1	180
75	5	0.5
	1	2
	0.1	81

Table 1: Influence of alkali concentration on aluminum consumption time.

So, Aluminum consumption was faster when the concentration of potassium hydroxide solution is higher. The best results were achieved for a 5M KOH solution at 75°C. In these conditions, 0.1g of Al were consumed in just 0.5 minutes. As a consequence, the average H₂ evolution rate reached ca. 260mL/min in this case. This result is noteworthy for such a small laboratory device.

3.3 Precipitation of Al(OH)₃

A new experiment was carried out using a KOH 5M solution prepared with deionized water, in order to compare the precipitate composition obtained using tap water or deionized water. Each solid fraction filtered was analyzed by X-Ray diffraction. Results are shown in Figures (2-3):

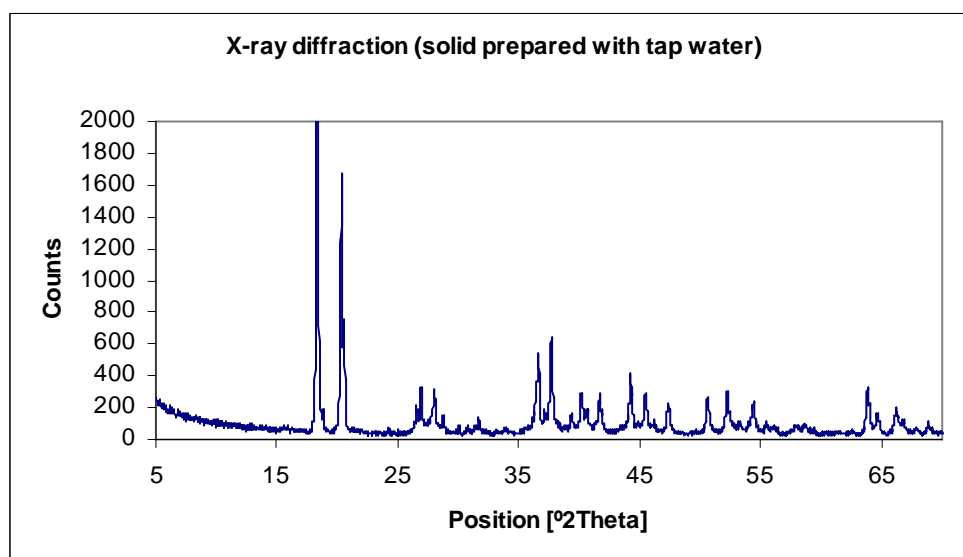


Figure 2: X-ray diffraction corresponding to solid filtered in tap water experiment.

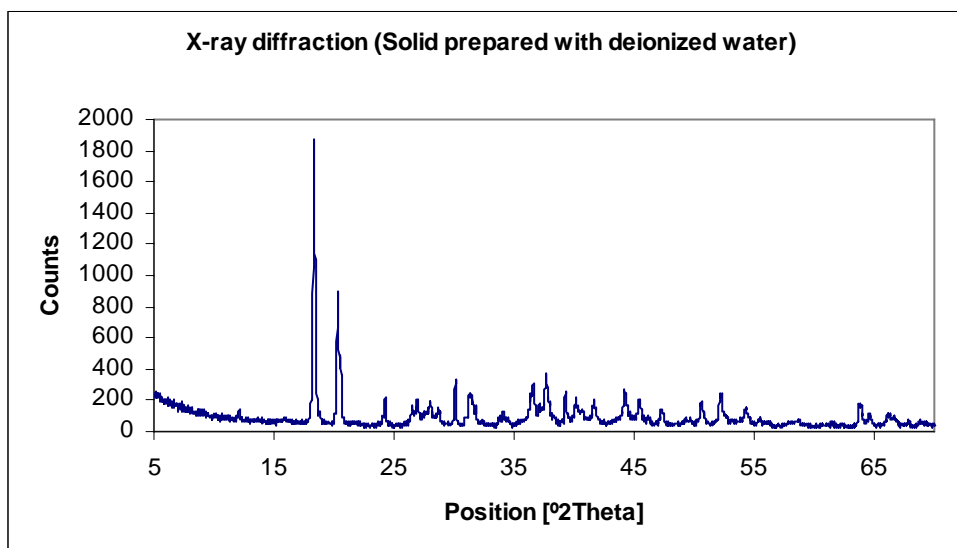


Figure 3: X-ray diffraction corresponding to solid filtered in deionized water experiment.

These results confirm that solid formed is basically composed by $\text{Al}(\text{OH})_3$ and potassium hydrogen carbonate. Alkaline solutions in contact with air react with atmospheric CO_2 to form aqueous CO_3^{2-} and HCO_3^- . Solid fractions prepared with tap water contained potassium hydrogen carbonate hydrate could be produced by rehydration of solid samples under atmospheric conditions for several days. Crystalline phases identified with X-Ray diffraction data base are reported in table 2.

Water purity	Compounds
Tap water	Gibbsite, syn. ($\text{Al}(\text{OH})_3$)
	Bayerite, syn. ($\text{Al}(\text{OH})_3$)
	Potassium hydrogen carbonate hydrate $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$
Deionized water	Gibbsite ($\text{Al}(\text{OH})_3$);
	Kalicinite, syn. KHCO_3

Table 2: Identified compounds with X-Ray diffraction peaks. (syn.= synthetic).

3.4 Long term experiment

Aluminum pieces in potassium hydroxide solution produce hydrogen following reaction (4). Six hydrogen generation runs were carried out consecutively, reusing the resultant alkaline solution every time, in order to confirm that KOH is regenerated (5). Initially, 200 ml of 5.0M KOH freshly prepared were used. Temperature evolution during first run and water additions versus time are shown in Figure 4. Note that tap water additions imply a decrease in solution temperatures, that were recovered later on. Experimental data of the six runs are reported in Table 3.

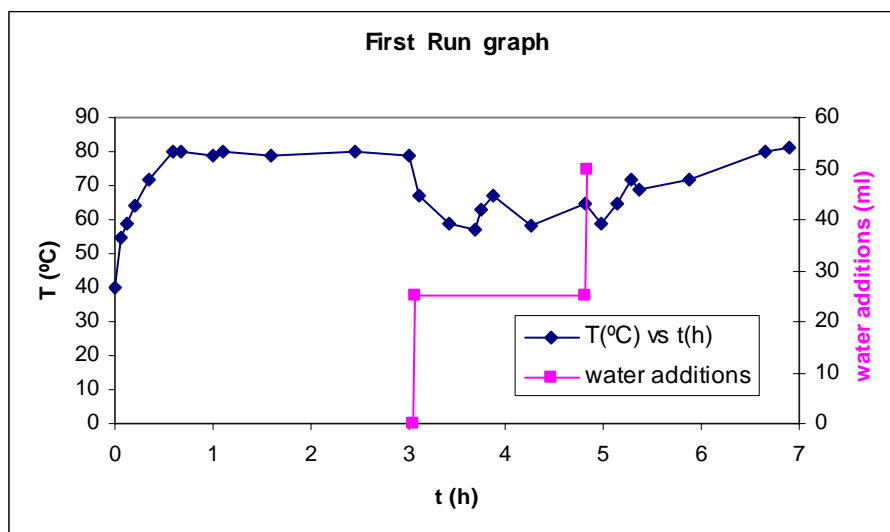


Figure 4: Temperature evolution and water addition for first hydrogen generation run.

Run	Al added (g)	Total water added (ml)	Solid produced (g)	Initial total alkalinity concentration (M)	Al consumption Accumulated (%)
1	43.1	50	109	5	160
2	30.5	245	96.3	a	273
3	44.2	215	126	a	437
4	31.2	85	83.9	3	552
5	28.0	125	87.9	3	656
6	17.4	25	44.3	3	721

Table 3: Experimental data of hydrogen generation runs (a=not measured).

At the end of sixth run, alkali solution was still reactive and it had a total alkalinity concentration of 3M. A new titration was performed in order to determine the free concentration (using phenolphthalein as end point indicator). Results showed that carbonate had a concentration of 1.54M and free alkalinity was only 0.03M. The measured pH of resultant alkaline solution was 13.9. This result is not surprising taking into account that the contact time of working solution with atmosphere was a total of two months. Therefore, CO₂ contributes to diminish free OH⁻ concentration and it is desirable to avoid its presence in further development of this process.

Aluminum consumption was calculated considering only reaction (4), which is equivalent to reaction (1) referred to NaOH. A total amount of 7.2 moles of aluminum were consumed per mol of KOH. This result shows that reaction (5) regenerates KOH and the global process is carried out by reaction (3), producing hydrogen with consumption of just water and aluminum.

In each run, it was observed that the rate of reaction (3) slowed to unacceptably low levels as solids content of alkaline solution approached 50% by weight. After filtration of alkaline solution, the rate of reaction is recovered in part, but process went slower in consecutive runs. Concretely,

at 25°C, at first run 0.1g Al were consumed in less than 3 minutes. However, at sixth run, at 25°C, approximately 12 minutes were needed to consume the same quantity. After the sixth run, 0.1g Al were consumed in 20 min at 25°C. Therefore, atmospheric carbonation is an important factor in hydrogen production by this way. Addition of enough aluminum to cover solution surface at once caused aluminum passivation instead of increasing hydrogen production. Aluminum passivation could be attributed at $\text{Al}(\text{OH})_3$ particles that are deposited at aluminum surface and make more difficult hydrogen generation.

In first runs, it was observed that part of precipitate was strongly adhered at the bottom of Pyrex vessel because of high solution alkalinity. So, another kind of material would be more suitable to carry out this reaction.

4. CONCLUSIONS

Production of hydrogen has been achieved using the reaction of aluminum with potassium hydroxide. Consumed raw materials are only tap water and aluminum. Therefore, this process represents an economic advantage respect hydrogen production using hydrides. The hydrogen production process reported is superstoichiometric, although part of potassium hydroxide was lost during the process, diminishing the reaction rate, due to atmospheric carbonation of alkaline solution to produce potassium hydrogen carbonate. Thus, in these conditions, this process was not fully catalytic. The best hydrogen production conditions found were at 75°C and using a 5M KOH solution. Hydrogen production reaction rate also diminished when increasing the solution solids content or when high amounts of aluminum were added to the alkaline solution.

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