

Reaction of Aluminum with Water to Produce Hydrogen

A Study of Issues Related to the Use of Aluminum for On-Board Vehicular Hydrogen Storage

U.S. Department of Energy



Version 2 - 2010

CONTENTS

EXECUTIVE SUMMARY	3
INTRODUCTION	5
BACKGROUND	5
REACTION-PROMOTING APPROACHES	6
Hydroxide Promoters	
Oxide Promoters	
Salt Promoters	
Combined Oxide and Salt Promoters	
Aluminum Pretreatment	
Molten Aluminum Alloys	
PROPERTIES OF THE ALUMINUM-WATER REACTIONS RELATIVE	14
TO ON-BOARD SYSTEM PROPERTIES	
Hydrogen Capacities	
Kinetic Properties	
System Considerations	
REGENERATION OF ALUMINUM-WATER REACTION PRODUCTS	17
SUMMARY	19
REFERENCES	20
APPENDIX I – THERMODYNAMICS OF ALUMINUM-WATER REACTIONS ...	23
APPENDIX II – ORGANIZATIONS PRESENTLY INVOLVED WITH	26
HYDROGEN GENERATION FROM ALUMINUM-WATER REACTIONS	

Reaction of Aluminum with Water to Produce Hydrogen

John Petrovic¹ and George Thomas²

Consultants to the DOE Hydrogen Program

¹ Los Alamos National Laboratory (retired)

² Sandia National Laboratories (retired)

Executive Summary:

The purpose of this White Paper is to describe and evaluate the potential of aluminum-water reactions for the production of hydrogen for on-board hydrogen-powered vehicle applications. Although the concept of reacting aluminum metal with water to produce hydrogen is not new, there have been a number of recent claims that such aluminum-water reactions might be employed to power fuel cell devices for portable applications such as emergency generators and laptop computers, and might even be considered for possible use as the hydrogen source for fuel cell-powered vehicles.

In the vicinity of room temperature, the reaction between aluminum metal and water to form aluminum hydroxide and hydrogen is the following: $2\text{Al} + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2$. The gravimetric hydrogen capacity from this reaction is 3.7 wt.% and the volumetric hydrogen capacity is 46 g H₂/L.

Although this reaction is thermodynamically favorable, it does not proceed due to the presence of a coherent and adherent layer of aluminum oxide that forms on the surface of aluminum particles which prevents water from coming into direct contact with the aluminum metal. The key to inducing and maintaining the reaction of aluminum with water near room temperature is the continual removal and/or disruption of this coherent/adherent aluminum oxide layer.

A number of reaction-promoting approaches have been investigated for the aluminum-water reaction. These include additions of hydroxide promoters such as NaOH, oxide promoters such as Al₂O₃, and salt promoters such as NaCl. These additions act to disrupt the aluminum oxide layer on the aluminum metal. In addition, the reaction of water with molten aluminum alloys such as aluminum-lithium and aluminum-gallium has been studied. In this case, the molten nature of the alloy prevents the development of a coherent and adherent aluminum oxide layer. However, none of these approaches have proven commercially viable to date.

The concept of using the aluminum-water reaction to provide onboard hydrogen for hydrogen-powered vehicles presents a number of difficulties. First, storage systems using this approach will not be able to meet the 2015 DOE system targets of 5.5 wt.% hydrogen and 40 grams hydrogen per liter. Second, based on published aluminum-water reaction rate kinetics, it appears

difficult for this approach to meet the DOE minimum hydrogen flow rate target for fuel-cell powered vehicles. Finally, the cost of producing hydrogen by this approach is dictated by the cost of aluminum metal. The March 2010 commodity price for aluminum is \$2.21 per kg. At this price, hydrogen from an aluminum-water hydrogen generation approach would cost approximately \$20 per kg H₂. Even assuming high volume production, the DOE target range for hydrogen cost of \$2-3 per kg H₂ would not be met. Additionally, the supply of aluminum required for mass market vehicle applications may be problematic.

While aluminum-water reaction systems cannot meet the targets for on-board vehicular hydrogen storage, the use of aluminum as a water splitting agent for generating hydrogen might have utility for non-vehicular applications.

Introduction:

The concept of producing hydrogen by the reaction of certain metals with water was first proposed in the late nineteenth century (1). In more recent times, a paper by Smith in 1972 described an approach using an amalgamated aluminum surface (2). In a 1976 U.S. Patent, Gutbier and Hohne indicated that hydrogen could be produced via the reaction of magnesium-aluminum mixtures with sea water (3). Since then, there has been renewed activity, reflected in a number of publications and patents directed at the production of hydrogen through reactions between aluminum-based metals and water. All of the aluminum-based approaches propose methods to circumvent the protective layer of aluminum oxide, thus allowing the reaction with water to proceed.

The hydrogen produced via such aluminum-water reactions might be employed to power fuel cell devices for portable applications such as emergency generators and laptop computers. There is also the suggestion that aluminum-water reactions might be used for hydrogen storage on fuel cell-powered vehicles. The purpose of this White Paper is to describe and evaluate the potential of aluminum-water reactions for the production of hydrogen, primarily aimed at on-board hydrogen-powered vehicle applications. We first discuss the aluminum-water reaction and describe the various methods devised to maintain the reaction. Then we consider the performance of such a system relative to the requirements for on-board vehicular hydrogen storage. Since any hydrogen generation concept, whether it is for on-board storage or not, will need to be regenerable (that is, the reaction products will need to be returned to the initial form of aluminum), the energy and cost requirements for these processes will be discussed.

Background:

The following are possible reactions of aluminum with water:



The first reaction forms the aluminum hydroxide gibbsite ($\text{Al}(\text{OH})_3$) and hydrogen, the second reaction forms the aluminum hydroxide boehmite ($\text{AlO}(\text{OH})$) and hydrogen, and the third reaction forms aluminum oxide and hydrogen. All these reactions are thermodynamically favorable from room temperature past the melting point of aluminum (660°C). All are also highly exothermic. From room temperature to 280°C , $\text{Al}(\text{OH})_3$ is the most stable product, while from 280 - 480°C , $\text{AlO}(\text{OH})$ is most stable. Above 480°C , Al_2O_3 is the most stable product (4). See the Appendix I for a more thorough review of the thermodynamics of aluminum-water reactions.

Table I: Thermodynamics of the aluminum-water reaction.

$2/3\text{Al} + 2\text{H}_2\text{O} = 2/3\text{Al}(\text{OH})_3 + \text{H}_2(\text{g})$			
T	ΔH	ΔS	ΔG
°C	kJ/mol H ₂	J/K	kJ/mol H ₂
0	-277	26.2	-284
100	-284	3.29	-285
200	-291	-12.1	-285

The reaction thermodynamics shown in Table I indicate that aluminum should spontaneously react with water. However, in practice a piece of aluminum dropped into water will not react under room temperature conditions, or even with boiling water. This is because the aluminum has a thin coherent, adhering layer of aluminum oxide, Al₂O₃, on its surface and this alumina layer prevents the reaction. So the key to inducing and maintaining the reaction of aluminum with water at room temperature is the continual removal and/or disruption of the hydrated alumina layer.

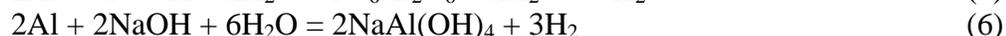
Organizations that are currently involved with the development of aluminum-water systems for the production of hydrogen are listed in Appendix II.

Reaction-Promoting Approaches:

Hydroxide Promoters:

A number of U.S. patents describe the use of hydroxides, primarily sodium hydroxide (NaOH), to promote aluminum-water reactions (5-9). There are two pertinent technical references on this subject. The first is by Belitskus (10). Here, experiments were described in which aluminum specimens including a cylindrical block, uncompacted powders, and pellets of various densities were reacted with aqueous solutions of sodium hydroxide at different concentrations to produce hydrogen gas at temperatures near room temperature. The formation of sodium aluminate was observed, as well as the regeneration of sodium hydroxide via the precipitation of aluminum hydroxide. Stockburger et.al. (11) described hydrogen generators in which aluminum was reacted with an aqueous solution of 5.75 M sodium hydroxide.

The types of reactions found to occur between aluminum, sodium hydroxide, and water are shown below:



One of the problems with the use of aqueous NaOH solutions is the corrosive nature of the liquid, which can lead to corrosion of system equipment. An example of a hydrogen-producing reactor based on the NaOH approach from a 2006 patent is shown in Figure 1.

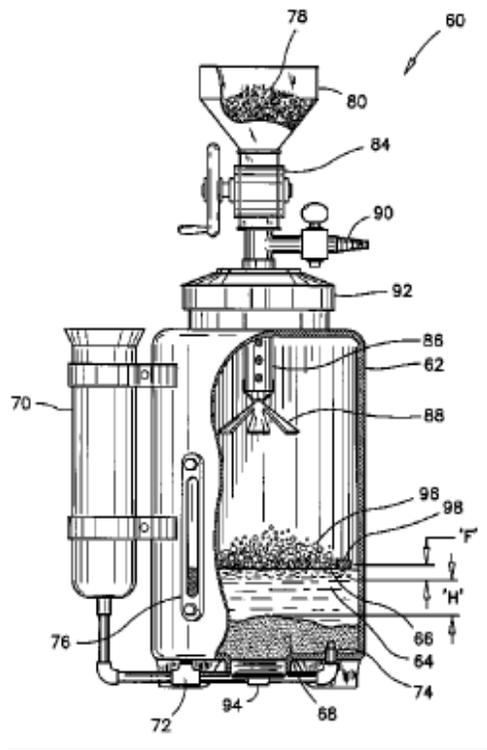


Figure 1: Hydrogen-producing reactor based on the NaOH approach (9).

Here, the aluminum powder is fed into the reaction chamber, where it reacts with the sodium hydroxide solution near room temperature, with the production of hydrogen gas and the formation of reaction byproducts at the bottom of the reactor. It is unclear whether this system has been commercially developed or utilized to date.

Oxide Promoters:

It has been shown that mixtures of aluminum and aluminum oxide (Al_2O_3) powders are reactive with water in the pH range of 4-9 (12-14) and at temperatures of 10-90 °C. These Al- Al_2O_3 powder mixtures must be heavily ball-milled together in order to produce hydrogen reactions. Hydrogen can be evolved at room temperature using essentially neutral water, although the hydrogen evolution rate increases with increasing temperature. An example of this effect is shown in Figure 2.

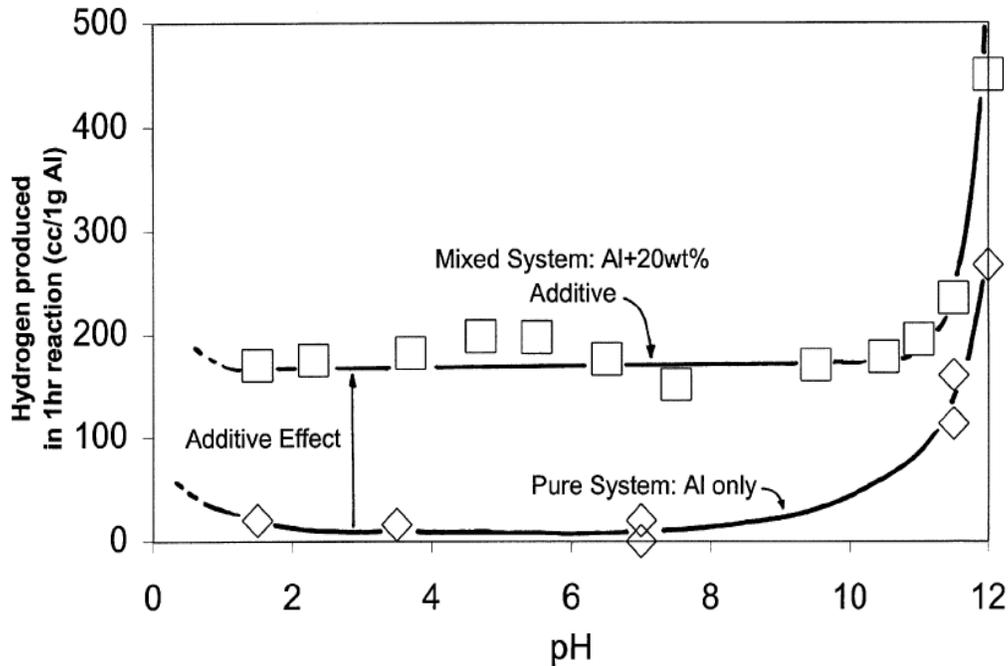


Figure 2: Hydrogen production versus pH for aluminum-aluminum oxide powder mixtures (13).

The aluminum oxide may be in the form of gibbsite ($\text{Al}(\text{OH})_3$), boehmite ($\text{AlO}(\text{OH})$), gamma alumina ($\gamma\text{-Al}_2\text{O}_3$), or alpha alumina ($\alpha\text{-Al}_2\text{O}_3$). Alpha alumina powder was reported to give the maximum hydrogen evolution.

It has been speculated that the milling of aluminum and aluminum oxide powders together helps to mechanically disrupt the adherent and coherent oxide layers present on the aluminum powder, and that this is the reason for the enhanced hydrogen generation in pH neutral water (12-14).

However, recent research has suggested that the enhancing effect of aluminum oxide on the reactivity of aluminum with water may also be mechanochemical in nature (15). Aluminum powders that were reacted with fine boehmite powders at elevated temperatures produced a layer of fine-grained, mechanically weak gamma alumina on the surfaces of the aluminum powders. As shown in Figure 3, this gamma alumina could then react with water to produce boehmite

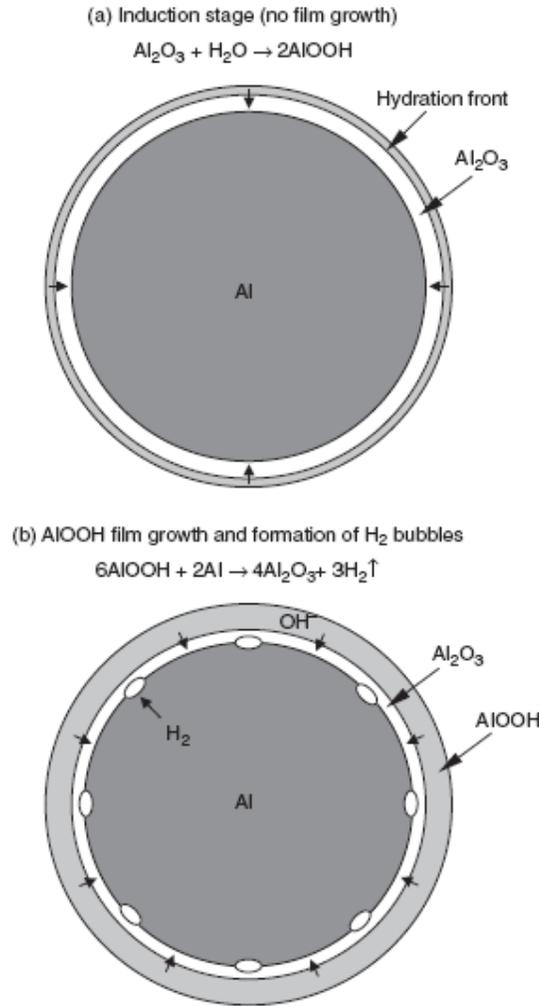


Figure 3: Reaction mechanism of water with an alumina-coated aluminum particle (15).

which would grow in thickness until the boehmite reacted with the underlying aluminum to produce hydrogen bubbles at the aluminum-boehmite interface. Under suitable conditions, these bubbles would then rupture the Al_2O_3 layer, leading to activation of the aluminum for reaction with water.

Salt Promoters:

Water soluble inorganic salts can produce localized pitting and rupture of the alumina layer on aluminum particles (16,17). Such effects have been employed to promote aluminum-water hydrogen production reactions (18,19). The salts NaCl and KCl were found to be the most effective. Powders of these salts were ball-milled together with aluminum powder in a 1:1

weight ratio. The resultant hydrogen generation when the ball-milled aluminum-salt mixture was exposed to water at 55 °C is shown in Figure 4.

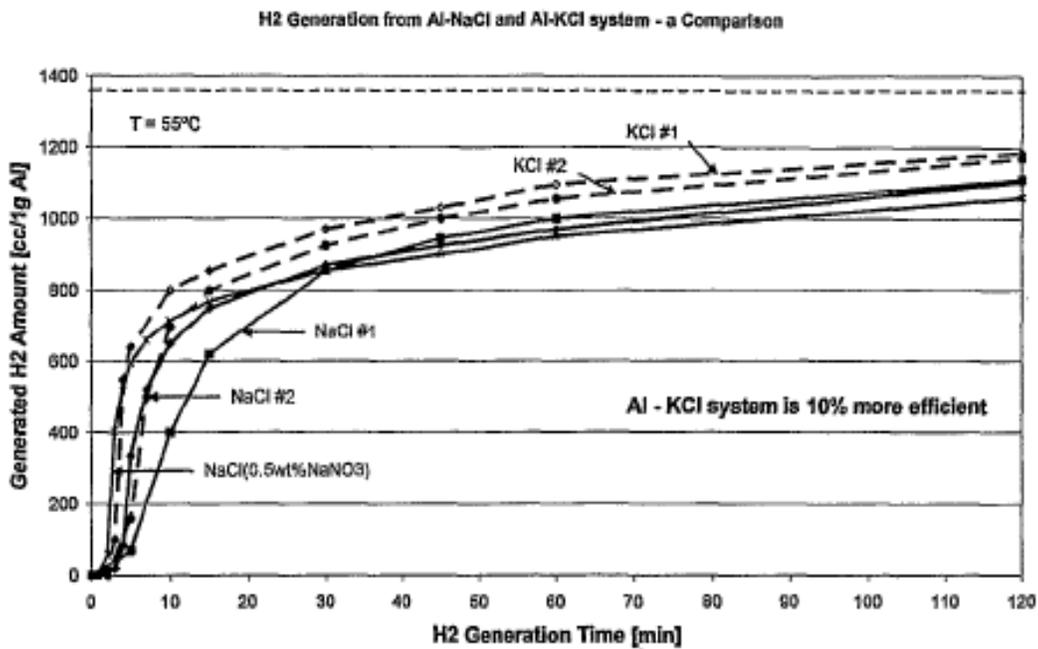


Figure 4: Reaction of aluminum-salt mixtures with water (18).

Reaction of the aluminum-salt mixtures with water was observed to be significantly temperature dependent, as shown in Figure 5.

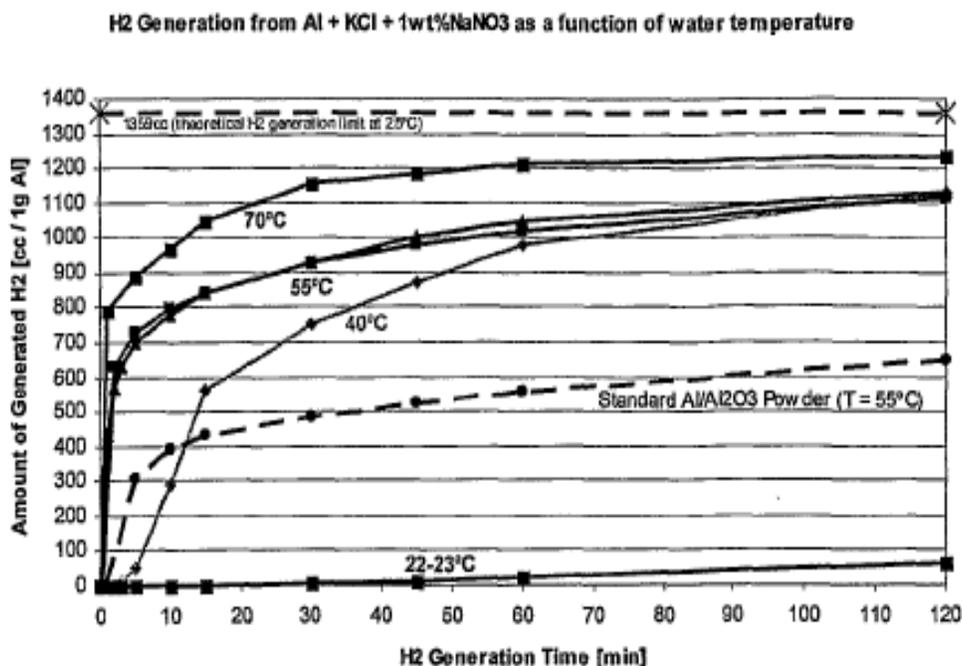


Figure 5: Effect of temperature on aluminum-salt reactions with water (18).

It has also been reported that if the salt is washed out of the aluminum powder at a lower water temperature, the aluminum powder will still react to produce hydrogen (19). In this case, the salt was washed out of the aluminum powder with cold tap water at 12 °C. Then the aluminum powder alone was immersed in water at 55 °C. This might suggest that milling the aluminum powder with the salt powder produces some disruption of the alumina layers on the aluminum particles, thus activating the aluminum for reaction with water.

Combined Oxide and Salt Promoters:

An international patent application (2006) has indicated that oxide and salt additions may be combined to promote the reaction of aluminum with water at 20 °C (20). The preferred oxide is calcium oxide in the range of 0.5 – 4 % by weight. The preferred salt is sodium chloride in a weight ratio of 1:1 with aluminum. Shown in Figure 6 are the hydrogen generation levels as a function of oxide addition. The hydrogen release kinetics indicated are relatively slow, with a maximum rate of only about 0.001 g H₂/sec under the specific generation conditions (e.g. amount of solution and catalyst) employed for the results in Figure 6.

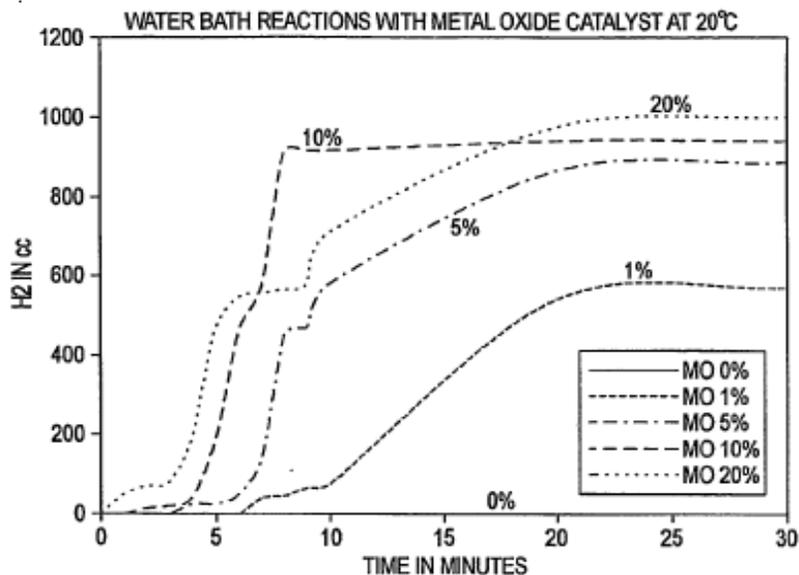


Figure 6: Hydrogen generation for different oxide level additions (20).

Aluminum Pretreatment:

A recent patent application has indicated that aluminum powders can be activated by ball-milling them in water, followed by a rapid heating and cooling thermal shock treatment (21). The improvement in hydrogen generation from the aluminum-water reaction is shown in Figure 7.

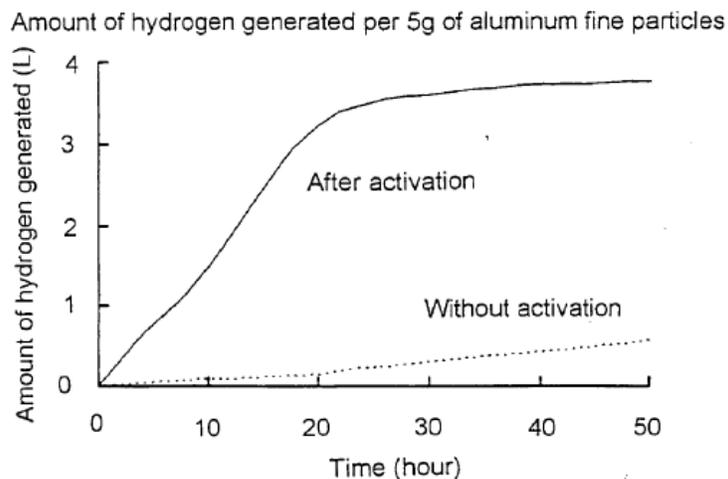


Figure 7: Effect of powder activation on hydrogen generation (21).

The hydrogen release rate from the activated aluminum powder is low, only of the order of 8×10^{-7} g H₂/sec/g of Al.

Molten Aluminum Alloys:

The reaction of water with molten aluminum alloys has been proposed. In one approach, molten aluminum-lithium alloys are sprayed with liquid water through a nozzle in a reaction chamber in order to generate hydrogen (22,23). A drawing of this reaction chamber is shown in Figure 8.

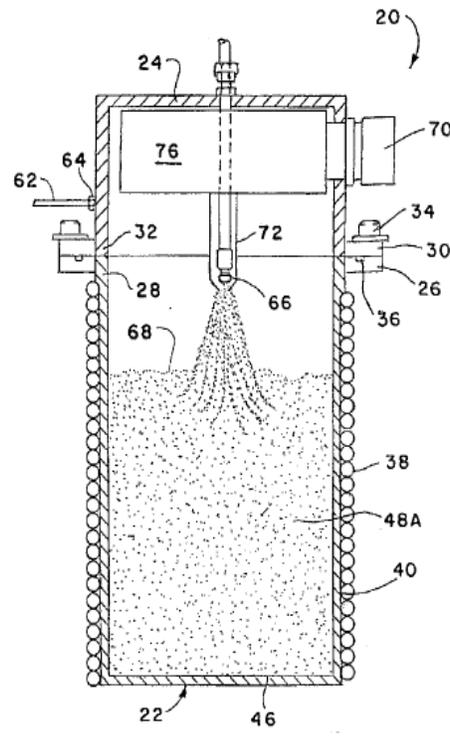


Figure 8: Reactor for hydrogen generation from molten aluminum-lithium alloys (22).

The reaction of molten aluminum-gallium alloys has also been suggested (24,25). The rationale here is that molten aluminum-gallium alloys will not possess a coherent and adherent oxide layer. Because no oxide layer is present on the liquid alloy, it will react readily with liquid water. Additionally, the aluminum-gallium alloys will have a low melting point range, as shown in Figure 9.

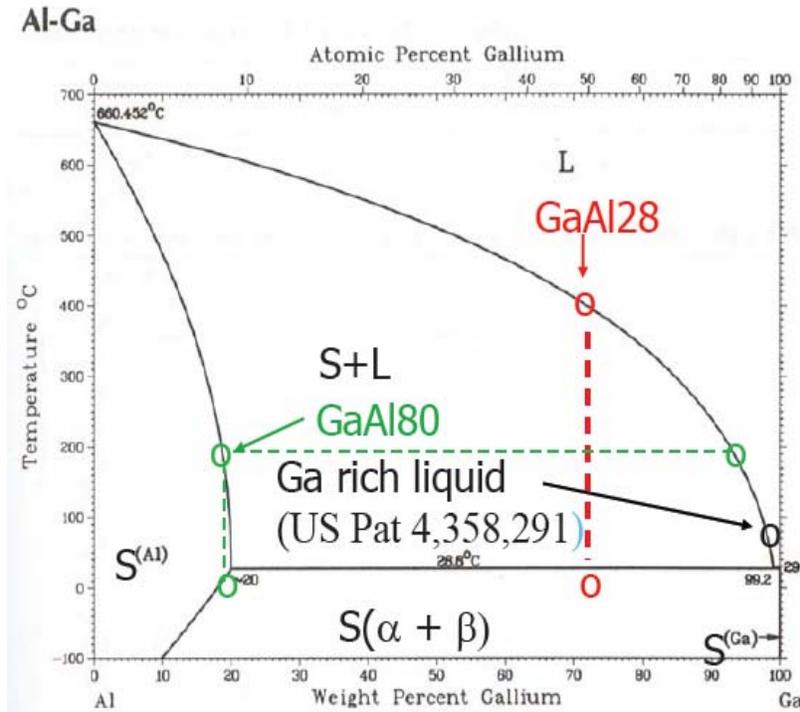


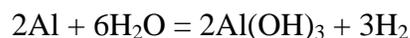
Figure 9: Aluminum-gallium phase diagram showing hydrogen-producing alloys (25).

In the hydrogen production process, the gallium would be essentially an inert species that could be reused. As may be seen in the aluminum-gallium phase diagram in Figure 9, the temperature at which the aluminum-gallium alloy is liquid increases with increasing aluminum content. However, the alloy is liquid below 100 °C only for gallium-rich mixtures where the aluminum content is only a few percent by weight. More recent work since the patent application [25] indicates that solid particles of Al 80%:Ga 20% by weight alloy could be formed by slow cooling a Ga –rich mixture (Al 28%:Ga 72%) from the melt. This aluminum rich alloy was found to react with water, but no information on reaction rates is available.

Properties of the aluminum-water reactions relative to on-board system properties:

Hydrogen Capacities:

One of the important parameters for on-board storage materials is their available hydrogen capacities in terms of weight and volume. The DOE capacity targets are system targets and include reactants, products, and all the balance-of-plant to contain them (including the tank), but here we consider the material capacities – a primary consideration to determine the feasibility of achieving system targets. The gravimetric capacity is usually quoted in wt.% of hydrogen and must include all reactants and/or reaction products. Since the formation of gibbsite is thermodynamically favored below 280 °C, we will only consider the reaction shown in Eq. (1):



The hydrogen gravimetric yield based on the aluminum alone without including the water, 11 wt.%, is not a relevant factor. Even if the water could be supplied by, for example, the fuel cell exhaust stream (an unlikely possibility (26)), the hydroxide reaction product remains on-board the vehicle and must be included in the weight. Thus, the theoretically best gravimetric density of hydrogen for this material reaction is 3.7 wt.%. In any practical system, most or all of the water will need to be stored as well and any alloying additions (such as gallium) or other reaction promoters (such as NaOH, NaCl, or Al₂O₃) will add more weight and further reduce the hydrogen weight density. Estimated values for some of the promoter schemes described earlier are given in Table II.

The material volumetric densities of hydrogen for the reactions can be estimated from knowledge of the material density and the hydrogen weight fraction. Thus, the left side of Eq. (1) corresponds to an overall material density of 1.26 g/mL and a weight density of 3.7 wt.% hydrogen. The volume density of hydrogen (for the materials only) is then ~ 46 g H₂/L. Volumetric capacities for the different schemes are also included in Table II.

Table II
Hydrogen Weight and Volume Capacities for Different Promoter Schemes

Material	Gravimetric capacity	Volumetric capacity
Pure aluminum	3.7 wt.% H ₂	46 g H ₂ /L
Hydroxide promoter	2.5 wt.% H ₂	36 g H ₂ /L
Oxide promoter	2.5 wt.% H ₂	40.6 g H ₂ /L
NaCl salt promoter	2.8 wt.% H ₂	39 g H ₂ /L
Ga 20/Al 80 alloy	3.0 wt.% H ₂	37 g H ₂ /L

Kinetic properties (hydrogen delivery rates):

The data shown for the various promoter schemes indicate that the water splitting reaction rate generally has strong temperature dependence. Also, since the reaction occurs at the metal surface, the hydrogen generation rate for a given system is related to the surface area of the aluminum particles in contact with the water. The experimental hydrogen production rates are usually reported in terms of the quantity of material, that is, g H₂/g of Al per unit time at a given temperature, but the material parameters (e.g., particle size or surface area) are not always given, making a comparison between some of the promoter schemes less meaningful.

There are a few cases that can be considered, however. The reaction rate shown in Figure 7 for the pretreated aluminum is quite low, at ~ 8 x 10⁻⁷ g H₂/sec/g of Al. Deng, et. al. (15) measured a hydrogen production rate of ~ 4 x 10⁻⁶ g H₂/sec/g of Al at 50 °C, using Al₂O₃ as a promoter. Using KCl and NaCl salts as promoters, Troczynski (18) measured a rate of ~ 2 x 10⁻⁴ g H₂/sec/g of Al at 55 °C. No reaction rate data is available at this time for the Al-rich Ga alloy.

A delivery rate of 1.6 g H₂/sec is required for an 80 kW vehicular fuel cell. At a kinetic reaction rate of 2 x 10⁻⁴ g H₂/sec/g of Al for the aluminum-water reaction (the maximum value in the

literature), one must react 8000 g of aluminum with the necessary amount of water in order to achieve the hydrogen delivery rate of 1.6 g H₂/sec needed to supply the 80 kW fuel cell. This makes it clear that the kinetics of aluminum-water reactions (at least those presently documented in the literature) are likely to be problematic for vehicular applications. These kinetic requirements are discussed further in the next section where system issues are considered.

System considerations

In addition to the material properties discussed above, there remain a number of issues related to actual use of the aluminum/water reaction onboard a vehicle to generate hydrogen for a fuel cell or ICE. These include: (1) containment of fresh reactants and the separation and storage of reaction byproducts; (2) components or subsystems to promote and control the generation of hydrogen in response to a highly transient fuel demand profile; (3) thermal management to control temperatures and energy, (4) loading of fresh material and unloading of reaction byproducts.

An important advantage of the proposed process is that containment of the materials is relatively straight forward, although the caustic nature of NaOH may require special consideration. Overall, however, it would appear that containers for the liquids and solids would most likely not be prohibitively heavy or expensive. The packing density of the solid metal particles would result in a volumetric density which typically is about 60% of the material density. Thus, the volume densities shown in Table I would be slightly lower (the density of the water remains the same regardless of the aluminum density). For example, the volumetric density for the pure aluminum case would be about 42 g H₂/L rather than 46 g H₂/ L.

The second issue, however, has a greater impact on the system parameters. In order to control the reaction (which runs to completion once started), either some metal or some water would need to be transported to a reactor. This is apparent in the patent proposals described in an earlier section of this paper which include schemes either for liquid or particle flow into a reaction chamber. The simplest case might be to control the rate of water flow to a container which holds all of the metal reactant.

Even then, the transient nature of the fuel demand on a vehicle would necessitate a buffer for retaining some quantity of hydrogen. The generation of 18 liters (STP) of hydrogen in one second (the volume equivalent of 1.6 gH₂) would require a container sufficiently large to accommodate the gas and a pressure rating to satisfy safety concerns. This fuel supply requirement, furthermore, would typically be required for more than just one second. Thus, an engineering approach might be a continuous water stream to maintain a roughly steady state hydrogen generation rate that is supplied to a buffer tank sufficiently large to satisfy the expected fuel rate requirements of the system. The buffer tank and the reaction chamber (and/or metal container) would need to be capable of retaining hydrogen at some reasonable pressure. Thus, the system weight and volume would be significantly larger than the material weights and volumes alone.

Thermal management is another system issue that cannot be ignored. The Al/water reaction is highly exothermic with an enthalpy of reaction of about 280 kJ/mol H₂ at ~50-100 C (see

Appendix I). At the peak hydrogen rate example cited above for an 80 kW fuel cell, the reaction would generate a heating power of about 225 kW. For the hydrogen buffer tank approach described above with an assumed steady state hydrogen generation rate of ~20% of full power, the average heat generation rate would be about 45 kW. This level of heat generation could be manageable, but would have to be considered in the system engineering design and would result in additional weight and volume. Due to the fact that heat rejection and radiator size are already issues in typical fuel cell system designs, the additional heat rejection may be considered a key disadvantage. Also, since the reaction rate is temperature dependent, some temperature control would be desirable to maintain the reaction bed at a preferred operating temperature, e.g., ~50 C.

Except for the occasional case of inadvertently running out of fuel, vehicles are always refueled before the fuel tank is fully emptied. Hence, an on-board hydrogen generation system might utilize most, but not all, of the metal reactant. Refueling in this case entails not only supplying more aluminum or alloy, but also the removal of the aluminum hydroxide reaction product. The straightforward approach proposed above, where the liquid is supplied to the metal container, results in a mixture of fresh and spent products. In this case, some method for separating out the reaction products from the unreacted aluminum on-board the vehicle will be required, so that these products can be discharged from the vehicle at the same time that it is refueled with fresh quantities of aluminum and water .

Regeneration of Aluminum-Water Reaction Products:

All of the promoter approaches result in the formation of aluminum hydroxide and it is this material that will need to be refined back to pure aluminum with very high efficiency for the process to be viable for hydrogen generation. Furthermore, any alloying species (such as gallium) or materials used to promote the reaction (such as NaOH or NaCl) must also be fully recoverable (or nearly so).

An excellent discussion of the process for primary aluminum production, as well as world-wide values for the energy requirements for aluminum smelting, can be found on a website produced by the International Aluminium Institute (www.world-aluminium.org). Briefly, the process is as follows:

Aluminum refining from aluminum-bearing bauxite ore uses the Bayer process chemistry which forms a hydrate which is essentially the same as the reaction product in the proposed aluminum-water reactions described above. The hydrate is then calcined to remove the water to form alumina. The alumina is electrolytically reduced into metallic aluminum at about 900 °C using the Hall-Heroult Process, producing a metal with 99.7% purity (see Figure 10). The smelting process requires continuous operation to be efficient. For 2005 (the latest figures reported by the Institute), the North American average energy used to reduce the oxide to the metal (smelting) is 15.552 kWh per kg of Al. This number does not include the energy used in mining and transporting the ore, the energy for processing the ore to the oxide, or the energy used in casting or carbon plants.

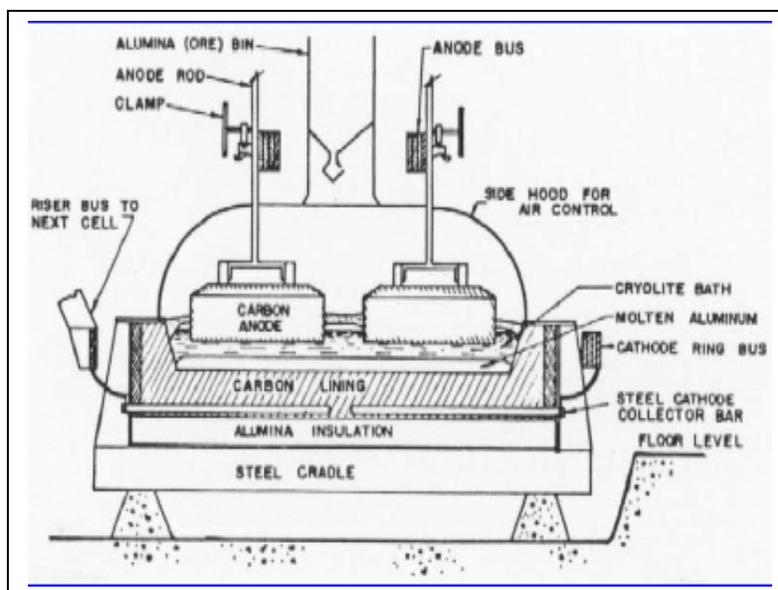


Figure 10: Schematic of the Hall-Heroult aluminum smelting process
(<http://electrochem.cwru.edu/ed/encycl>)

A regeneration loop for the spent material in the proposed hydrogen generation schemes would be essentially similar. The reaction product would first be calcined to remove the water and form alumina, Al_2O_3 . This would then be reduced electrolytically to metallic aluminum. Thus, the energy requirement quoted above would also apply to the present application, assuming a large facility that would be operated continuously. This energy would not include that needed for collecting, separating, and shipping the reaction products of the water reaction, calcining the material or for returning the metal to the point of use. It can provide an indicator, however, for comparing hydrogen generation costs to other methods and to the DOE targets.

At a weight fraction of 3.7 wt.% H_2 , the aluminum water splitting reaction generates one kg of hydrogen through the consumption of 9 kg of Al (assuming 100% yield). Using a value of 15.552 kWh per kg Al, the energy required to produce 1 kg of hydrogen would then be 140 kWh, or 500 MJ. Since the energy content of 1 kg of hydrogen is 120 MJ (lower heating value of hydrogen), the overall energy efficiency for hydrogen obtained using aluminum produced by the Hall-Heroult electrolytic process is 24%.

The cost of hydrogen generated by the Hall-Heroult process depends on the cost of electricity. The average wholesale price for electricity in the U.S. in 2005 was 5.05 cents per kWh (27). Using this value, the electricity cost alone to produce 1 kg of hydrogen from 9 kg of aluminum is \$7/kg H_2 . The actual cost of hydrogen produced from aluminum water splitting will undoubtedly be higher than this, due to additional costs associated with transporting material for reprocessing and back again for refueling, as well as for preparing the hydroxide for the aluminum smelting operation. For example, the March 2010 commodity price for aluminum is \$2.21/kg, which would translate into a hydrogen cost of \$20/kg H_2 if the aluminum commodity price were employed.

Another factor that should be considered is the amount of aluminum that would be required to produce hydrogen for large numbers of hydrogen-fueled vehicles. It is estimated that the fueling of 300 million vehicles would require 64 million metric tons of hydrogen per year. Since it requires 9 tons of aluminum to produce 1 ton of hydrogen through the aluminum-water reaction, this means that the fueling of 300 million vehicles would require 575 million metric tons of aluminum per year. To put this number in perspective, the world-wide production of aluminum in the year 2006 was 24 million metric tons (www.world-aluminium.org). Thus, the hydrogen fueling of very large numbers of vehicles via the aluminum-water reaction would require an expansion of world-wide aluminum production by approximately a factor of 25. In addition to the capital cost of new aluminum smelting facilities, the electricity consumption for aluminum production would have to increase by a similar factor.

Summary:

The key aspects associated with the production of hydrogen using the aluminum-water reaction are:

Aluminum Required: 9 kg Al per kg H₂ assuming 100% yield

Gravimetric Hydrogen Capacity: 3.7 wt.% (materials only)

Volumetric Hydrogen Capacity: 36-46 kg H₂/L (materials only)

Reaction Kinetics: 2×10^{-4} g H₂/sec/g of Al – from published data to date

Cost: \$7 per kg H₂ (based on the cost of electricity for aluminum production considering only the reduction of alumina to aluminum step)

It should be emphasized that the hydrogen capacity values given in this paper for the aluminum-water reactions are for the materials only. There are, in addition, a number of on-board system requirements that would add more weight and volume. Some examples are containers for the fresh materials and the reaction products, a mechanism for unloading spent materials and loading fresh materials, a reactor that would allow controlled quantities of materials to react, devices for transporting solid and/or liquid materials between the different components, water recovery sub-systems (if used), heat exchangers, pressure control valves, etc. Some of these system components may prove to be very difficult to design and fabricate for reliability and longevity. The highly transient behavior of the fuel requirements for vehicles would be particularly difficult to accommodate with a chemical system that, once started, runs to completion. This is very different from a metal hydride, for example, where the thermodynamics of the material both supply and limit the equilibrium hydrogen pressure at a given temperature.

The current DOE 2015 hydrogen storage system capacity targets are a hydrogen gravimetric capacity of 5.5 wt.% and a hydrogen volumetric capacity of 40 g H₂/L (28). It is clear from the analysis presented in this White Paper that no aluminum-water reaction system can meet these targets. Additional negative factors are the high cost of hydrogen from this process, and the amount of aluminum required for large-scale vehicular applications.

While such systems cannot meet the requirements for on-board vehicular hydrogen storage, the use of aluminum as a water splitting agent for generating hydrogen may have utility for non-vehicular applications, such as fixed-site electrical generators and electronic devices. The critical issues in these cases will be the modularity, the cost of such aluminum-water systems, and the economics of the delivered energy content relative to other fuel systems.

Acknowledgments:

The authors would like to thank Mr. Charles Knechtel for useful input in revising and improving this White Paper.

References:

1. G.F. Barker, "On Alloys of Gallium and Aluminum", The American Journal of Science, eds. J.D. Dana, E.S. Dana, and B. Silliman, vol. XIX, nos. 109-114, 65 (1880).
2. I. E. Smith, Hydrogen generation by means of the aluminum/water reaction; Journal of Hydronautics (1972), vol. 6, #2, 106-109
3. U.S. Patent 3,932,600; Process for the generation of hydrogen; January 13, 1976; Inventors: Heinric Gutbier, Karl Hohne; Assignee: Siemens Aktiengesellschaft.
4. M. Digne, P. Sautet, P. Raybaud, H. Toulhoat, E. Artacho, Structure and Stability of Aluminum Hydroxides: A Theoretical Study", J. Phys. Chem. B, 106, 5155-5162 (2002).
5. U.S. Patent 4,308,248; Material and method to dissociate water; December 29, 1981; Inventor: Eugene R. Anderson; Assignee: Horizon Manufacturing Corporation.
6. U.S. Patent 6,506,360; Method for producing hydrogen; January 14, 2003; Inventors: Erling Reidar Andersen, Erling Jim Andersen; Assignee: None listed
7. U.S. Patent 6,638,493; Method for producing hydrogen; October 28, 2003; Inventors: Erling Reidar Andersen, Erling Jim Andersen; Assignee: None listed
8. U.S. Patent 6,800,258; Apparatus for producing hydrogen; October 5, 2004; Inventors: Erling Reidar Andersen, Erling Jim Andersen; Assignee: None listed
9. U.S. Patent 7,144,567; Renewable energy carrier system and method; December 5, 2006; Inventor: Erling Jim Andersen; Assignee: None listed
10. D. Belitskus, "Reaction of Aluminum With Sodium Hydroxide Solution as a Source of Hydrogen", J. Electrochem. Soc., 117, 1097-1099 (1970).

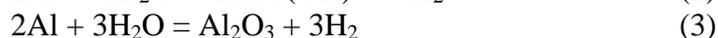
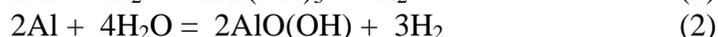
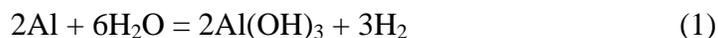
11. D. Stockburger, et.al., "On-Line Hydrogen Generation from Aluminum in an Alkaline Solution", Proc. Symp. Hydrogen Storage, Electrochem. Soc., 43, 1-44 (1992).
12. International Patent Application PCT/CA2001/001115; Hydrogen generation from water split reaction; February 21, 2002; Inventors: Asoke Chaklader, Das Chandra; Assignee: The University of British Columbia.
13. U.S. Patent 6,440,385; Hydrogen generation from water split reaction; August 27, 2002; Inventor: Asok C.D. Chaklader; Assignee: The University of British Columbia.
14. U.S. Patent 6,582,676; Hydrogen generation from water split reaction; June 24, 2003; Inventor: Asoke Chandra Das Chaklader; Assignee: The University of British Columbia.
15. Z-Y Deng, J.M.F. Ferreira, Y. Tanaka, and J. Ye, "Physicochemical Mechanism for the Continuous Reaction of γ -Al₂O₃-Modified Aluminum Powder with Water", J. Am. Ceram. Soc., 90, 1521-1526 (2007).
16. A.G. Munoz and J.B. Bessone, "Pitting of aluminum in non-aqueous chloride media", Corrosion Science, 41, 1447- 1463 (1999).
17. E. McCafferty, "Sequence of steps in the pitting of aluminum by chloride ions", Corrosion Science, 45, 1421-1438 (2003).
18. International Patent Application PCT/CA2005/000546; Compositions and methods for generating hydrogen from water; October 20, 2005; Inventors: Tomasz Troczynski, Edith Czech; Assignee: The University of British Columbia.
19. International Patent Application PCT/CA2006/001300; Microporous metals and methods for hydrogen generation from water split reaction; February 15, 2007; Inventors: Tomasz Troczynski, Edith Czech; Assignee: The University of British Columbia.
20. International Patent Application PCT/US2006/000180; Method and composition for production of hydrogen; July 6, 2006; Inventor: Jasbir Kaur Anand; Assignee: Hydrogen Power, Inc.
21. U.S. Patent Application 20060034756; Method for generating hydrogen gas utilizing activated aluminum fine particles; February 16, 2006; Inventors: Maseo Watanabe, Ximeng Jiang, Ryuichi Saito; Assignee: Dynax Corporation.
22. U.S. Patent 5,634,341; System for generating hydrogen; June 3, 1997; Inventors: Martin Klanchar, Thomas G. Hughes; Assignee: The Penn State Research Foundation.
23. U.S. Patent 5,867,978; System for generating hydrogen; February 9, 1999; Inventors: Martin Klanchar, Thomas G. Hughes; Assignee: The Penn State Research Foundation.

24. U.S. Patent 4,358,291; Solid state renewable energy supply; November 9, 1982; Inventors: Jerome J. Cuomo, Jerry M. Woodall; Assignee: International Business Machines Corporation.
25. J.M. Woodall, "The Science and Technology of Aluminum-Gallium Alloys as a Material for Hydrogen Storage, Transport and Splitting of Water", Keynote Address, ECHI-2 Conference, April 12, 2007, Purdue University.
26. Tarek-Abdel Baset, "Systems Approach to On-Board Hydrogen Storage Systems", Chrysler Corporation presentation in the Focus Session on High-Density Hydrogen Storage for Automotive Applications: Materials and Methods, Materials Science & Technology 2007 Conference, September 16-20, 2007, Detroit, Michigan.
27. DOE Energy Information Administration, Form EIA-861, Annual Electric Power Industry Report (<http://www.eia.doe.gov/cneaf/electricity/wholesale/wholesalet2.xls>).
28. http://www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html

Appendix I

Thermodynamics of Aluminum-Water Reactions

The possible reactions of aluminum with water are the following (4):



The first possible reaction product is $\text{Al}(\text{OH})_3$ (gibbsite). The second possible reaction product is $\text{AlO}(\text{OH})$ (boehmite). The third possible reaction product is Al_2O_3 (alumina). These reaction products differ in their level of hydration. All three of them produce the same amount of hydrogen with respect to the amount of aluminum reacted, but they differ in the amount of water that is required for the reaction. These reactions are all thermodynamically favorable over a wide temperature range from room temperature to temperatures far in excess of the melting point of aluminum (660 °C). In addition, all of these reactions are highly exothermic.

Table A1: Thermodynamic data for the aluminum-water reaction to form gibbsite.

$2/3\text{Al} + 2\text{H}_2\text{O} = 2/3\text{Al}(\text{OH})_3 + \text{H}_2(\text{g})$			
T	ΔH	ΔS	ΔG
C	kJ/mol H₂	J/K	kJ/mol H₂
0	-277	26.2	-284
100	-284	3.29	-286
200	-291	-12.1	-285
300	-298	-25.1	-283
400	-306	-38.0	-280
500	-316	-51.8	-276
600	-328	-66.8	-270
700	-350	-90.9	-262
800	-369	-109	-252
900	-391	-128	-240
1000	-417	-149	-232

Table A2: Thermodynamic data for the aluminum-water reaction to form boehmite.

$2/3\text{Al} + 4/3\text{H}_2\text{O} = 2/3\text{AlO}(\text{OH}) + \text{H}_2(\text{g})$			
T	ΔH	ΔS	ΔG
C	kJ/mol H₂	J/K	kJ/mol H₂
0	-267	83.3	-289
100	-279	39	-294
200	-285	26.6	-297
300	-291	13.8	-299
400	-302	-2.69	-300
500	-312	-17.4	-299
600	-323	-30.5	-296
700	-341	-49.9	-292
800	-352	-60.3	-287
900	-362	-69.8	-280
1000	-373	-78.5	-273

Table A3: Thermodynamic data for the aluminum-water reaction to form alumina.

$2/3\text{Al} + \text{H}_2\text{O} = 2/3\text{Al}_2\text{O}_3 + \text{H}_2(\text{g})$			
T	ΔH	ΔS	ΔG
C	kJ/mol h₂	J/K	kJ/mol h₂
0	-272	62.1	-289
100	-275	51.1	-294
200	-279	43.1	-299
300	-283	35.5	-303
400	-288	27.3	-306
500	-294	18.1	-308
600	-303	7.80	-310
700	-320	-11.3	-309
800	-333	-23.7	-308
900	-348	-37.1	-305
1000	-366	-51.6	-304

The thermodynamic parameters for the $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, and Al_2O_3 reactions are given in Tables A1, A2, and A3 as a function of temperature, using HSC Thermodynamic Software, Version 6.1.

For all these reactions, the enthalpy is highly exothermic, with an average value of -279 kJ/mol H_2 at 100°C and -337 kJ/mol H_2 at 700°C . One may also see that Al_2O_3 becomes more thermodynamically favorable than $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$ at elevated temperatures.

The free energy of the aluminum hydroxides compared to aluminum oxide is shown in Figure A1 below (4):

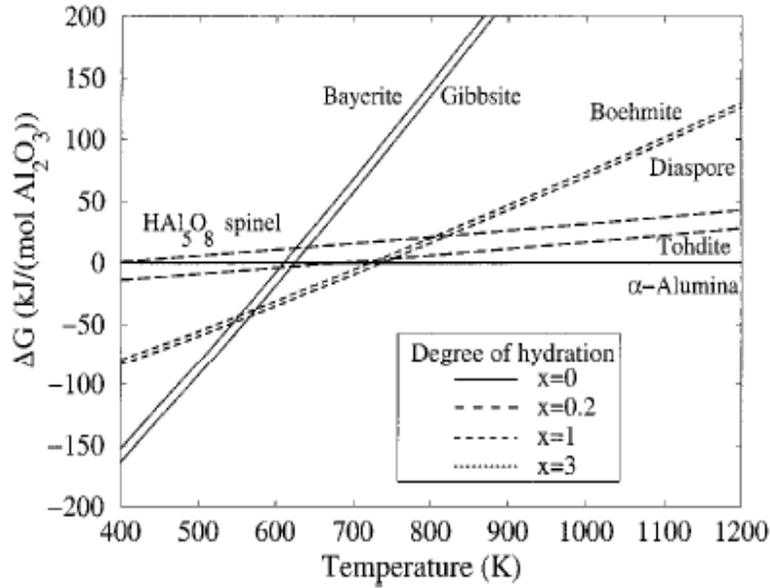


Figure 6. Gibbs free energy of the aluminum hydroxides compared to $\alpha\text{-Al}_2\text{O}_3$ (see eq 3), as a function of temperature and for different aluminum hydroxides. The energy is expressed per Al_2O_3 formula unit.

TABLE 8: Thermodynamical Stability of Aluminum Hydroxides (See Text for Definitions)

compound	unit cell $y[\text{Al}_2\text{O}_3, x\text{H}_2\text{O}]$	$\Delta G(298 \text{ K})$ (kJ/(mol Al_2O_3))	T_{inv} (K)	T_{exp}^a (K)
α -alumina	$2[\text{Al}_2\text{O}_3, 0\text{H}_2\text{O}]$	0		
tohdite	$5[\text{Al}_2\text{O}_3, 0.2\text{H}_2\text{O}]$	-17.7	698	> 900
boehmite	$2[\text{Al}_2\text{O}_3, \text{H}_2\text{O}]$	-97.5	719	> 720
diaspore	$2[\text{Al}_2\text{O}_3, \text{H}_2\text{O}]$	-101.4	731	770
bayerite	$8[\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}]$	-206.8	609	> 500
gibbsite	$8[\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}]$	-217.5	624	> 570

Figure A1: Thermodynamic stability of aluminum hydroxides versus temperature (Figure 6 and Table 8 from Reference 4).

It should be noted that both gibbsite and bayerite are different polymorphic forms of the aluminum hydroxide $\text{Al}(\text{OH})_3$ (gibbsite is slightly more thermodynamically stable than bayerite). As may be seen, from room temperature to 280 °C, $\text{Al}(\text{OH})_3$ is the most stable product, while from 280-480 °C, $\text{AlO}(\text{OH})$ is most stable. Above 480 °C, Al_2O_3 is the most stable product. This means that the stable product of the reaction of aluminum with water at room temperature will be the aluminum hydroxide $\text{Al}(\text{OH})_3$.

Appendix II
Examples of Organizations Presently Involved With Hydrogen Generation From
Aluminum-Water Reactions

Organization	Product	Website
Hydrogen Power Inc.	AlumiFuel Cartridge	http://www.hydrogenpowerinc.com
Altek Fuel Group Inc.	Hydrogen Fuel Cartridge	http://www.altekfuel.com
Purdue University	Aluminum-Gallium Alloys	http://hydrogen.ecn.purdue.edu/
HydPo Ltd.	Hydrogen from aluminum-water reaction	No website available Email contact: yossi@hydpo.com