Naval Research Laboratory
Washington, DC 20375-5320

NRL/6170/MR—2021/6

Assessment of Conceptual Systems Using Hydrogen Produced from the Reaction of Aluminum Alloys with Water

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March 24, 2021

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
24-03-2021

2. REPORT TYPE
NRL Memorandum Report

3. DATES COVERED *(From - To)*
08/01/2019 – 02/01/2021

4. TITLE AND SUBTITLE
Assessment of Conceptual Systems Using Hydrogen Produced from the Reaction of Aluminum Alloys with Water

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
8723

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

EGHimes Consulting
4 Coach Side Lane
Pittsford, NY 14534-9413

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL/6170/MR--2021/6

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
875 North Randolph Street
Arlington, VA 22217-1995

10. SPONSOR / MONITOR'S ACRONYM(S)
ONR

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
*USMC Marine Corps Military Liaison, Naval Research Laboratory 4555 Overlook Ave., S.W., Washington, DC 20375-5320
**EGHimes Consulting, 4 Coach Side Lane, Pittsford, NY 14534-9413

14. ABSTRACT

Hydrogen technologies, such as fuel cells, might improve the capability of the military. There is concern about the logistics and safety of transporting and using compressed hydrogen gas fuel, so some have proposed to react aluminum alloys with water for safe on-site hydrogen generation, as aluminum alloys are stable, safe to ship, and the water might found in the field. Our study finds that aluminum alloys as a "fuel" has only niche applications, because it is not energy dense at a system level. The aluminum/water reaction for hydrogen is not attractive except for a few niche applications, such as small weather balloons and small fuel cells for unmanned air vehicles or battery recharging.

15. SUBJECT TERMS
Hydrogen Fuel cells Aluminum alloys

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	UU	50	Karen S. Lyons
					19b. TELEPHONE NUMBER *(include area code)* (202) 834-0610

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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1.0 Executive Summary

Hydrogen fuel cells and other hydrogen technologies might improve the capability of the military and commercial applications, however there is concern about the logistics and safety of transporting and using compressed hydrogen gas fuel. As an alternative, some have proposed to react aluminum alloys with water for safe on-site hydrogen generation, as aluminum alloys are stable, safe to ship, and the water might found in the field. Some mechanisms have even been proposed to harvest aluminum scrap metal in the field, and use it to create hydrogen in a reactor. The hydrogen could then be used for stratospheric balloons or in combination with a fuel cell to make electricity, with almost no logistics tail.

The objective of this study is to provide a feasibility assessment of systems based on hydrogen generation from aluminum alloys, and the value of hydrogen/aluminum, specifically to missions relevant to the U. S. Marine Corps (USMC)

The following four application cases are evaluated herein:

1. Small Scale Standalone Hydrogen Generation/ Dispensing System for small balloons or unmanned air vehicles
2. Small Portable Power Recharging for battery systems
3. Large Scale Standalone Generation/ Dispensing System for Light duty Vehicles, Other Fuel Cell based System Fueling
4. Medium Mobile Power Generation for Mobile generators

The key criteria used to evaluate application feasibility include:

- the maturity/readiness of the technology
- potential capability of alternate/competing technologies
- logistics burden for use of the technology (weight, volume, estimated cost)
- thermodynamic/practical system limits of the technology
- Our own estimates of the weight of full energy generation systems.
- The cost of the technology

The results in Table I show that application 1 (small-scale standalone hydrogen generation) may be an attractive use of hydrogen generation from aluminum alloys, but application 4 (mobile power generation) is not a good use of the technology and is not recommended. The other applications for portable power generation and large scale stand-alone generation lie in between, and may have possible benefit.

Our main finding is that aluminum alloys as a "fuel" has only niche applications, because it is not energy dense at a system level. The energy density and specific energy of aluminum is often quoted as 83.8 MJ/L and 31 MJ/kg (or 3x that of diesel fuel), respectively. However, this is the total energy of the heat and hydrogen released from the aluminum reactant, while only the hydrogen byproduct should be considered the fuel. The weight and volume of the water reactant mass and volume must also be considered where it must be carried/transported, or stored on-board for mobile applications. Our analysis considers the weight and volume of the reactor needed to make the hydrogen, plus the energy conversion system, such as a fuel cell or engine, used to make practical energy. Due to the system complexity required to convert aluminum into electrical power, we find that the aluminum/water reaction for hydrogen is not attractive except for a few niche applications.

Future detailed studies and conceptual operations might reveal other opportunities for generating energy effectively from aluminum/water. The system might be improved by tailoring the aluminum to operate impure waste water that can be scavenged; developing/benchmarking optimal aluminum fuel fuels; quantifying actual reaction water consumption, and mechanisms affecting it; and thermodynamic modeling to inform the reactor controls and reactor design/development optimization.

Case Study	**H2 Quantity**	**Applications**	**Potential Application Feasibility**	**Potential Capability of Alternative Technologies**
Small Scale Standalone Hydrogen Generation/ Dispensing System	2-4 kg/day	Small Balloons or UAVs	Capable of quickly producing hydrogen in the battlefield, can combine multiple units for higher H_2 kg/day	• Bulk cylinder-stored (K,T bottles) hydrogen is a much heavier option with negative logistics impacts and safety concerns • Water electrolysis is possible, but requires electrolyzer systems, and sufficient power generation, and JP8 fuel at point of use
Small Portable Power Recharging	<0.1 kg/re-charge	Battery Recharging	Would offset extra carried batteries with a small, quiet, and light weight battery charger	• If small scale hydrogen generation/ compression is available, then gas refillable canisters could be a better alternative for hydrogen supply • Needs to be benchmarked against other fuel cell recharging systems available in the market place
Large Scale Standalone Generation/ Dispensing System	5-50 kg/day	Light duty Vehicles, Other Fuel Cell based System Fueling	Technically feasible alternative to diesel-fueled electrolysis systems, further comparative analysis required of equipment footprint, and logistic options	• Water electrolysis is a more mature alternative, and likely more cost effective, but requires sufficient power generation infrastructure and JP-8/diesel fuel availability
Medium Mobile Power Generation	~2 kg/refuel	Mobile generators	Inferior for power-only applications, considerable research still required to assess secondary uses for reaction heat	• Diesel generators are superior, improving with hybridization, and could also offer combined heat-and-power alternatives

Table I: Feasibility of aluminum-generated hydrogen for four different military and commercial missions.

2.0 Introduction

The U.S. Marine Corps is pivoting toward operation in austere, contested environments, requiring reimagining how missions will be carried out with limited communications and logistics resupply. One new useful technology might be hydrogen fuel cells, which are now robust and commercially available in the 50 W to 100 kW range – suitable for small portable power charging, light duty vehicle propulsion, quiet and clean back up power generation, and for long endurance unmanned air vehicle electric propulsion.

The use of hydrogen fuel cells requires the availability of hydrogen (H_2), which is presently not a logistics fuel and can be difficult to obtain commercially. While hydrogen logistics might seem contrived, hydrogen can be made anywhere that electricity and water are available, using commercial electrolysis equipment that uses electricity to split water into hydrogen and oxygen. The hydrogen usually has to be dried, and compressed for storage, so a dryer and compressor are needed as well.

Hydrogen can also be used as the lift gas for balloons for weather collection, atmospheric sensing, and communications. This is a particularly attractive application, as hydrogen could be made on site for rapid inflation of balloons, without a reliance on importing helium. Hydrogen is used routinely as a lift gas now for commercial weather monitoring.

Due to the draw of hydrogen technologies, an alternative source of hydrogen has been proposed from the direct reaction of water with high surface area aluminum-alloy fuel pellets/powder. The generation of hydrogen from aluminum alloys has been researched for years, and the viability of the technology has been rejected for automotive applications by the U.S. Department of Energy (DOE) [1]. They found that the generation of hydrogen from aluminum alloys was not viable onboard a vehicle, because the systems could not meet the DOE targets of hydrogen gravimetric capacity of 5.5 wt.% and a hydrogen volumetric capacity of 40 g H_2/L when considering total volume required for the reactants (water + aluminum), reactor, and the system balance of plant (BOP). The high cost of generating hydrogen from reacting with aluminum was found to be another detractor. However, the authors speculated that there might be limited use of the technology for fixed-site electrical generators and electronic devices, if the cost and delivered energy content of the systems were attractive.

We study the merit of aluminum alloys as a generation source for hydrogen for military and niche commercial applications, where the cost of the fuel is less of a concern. Significant research has been carried out on aluminum alloy-water hydrogen generation since the DOE report in 2010, and new alloys and systems have been created that use the aluminum fully and effectively, without losses to side reactions. Aluminum alloy formulations have also been developed to prevent the rapid activation of the aluminum in air and make it safe to handle and store.

This report gives an overview of the materials and reactor conditions needed for efficient hydrogen generation from aluminum alloys. We consider a conceptual hydrogen reactor, and carry out analysis of the effectiveness of hydrogen production from water for different systems. Literature values, and our own experience, are used to accurately size the systems.

Manuscript approved March 2, 2021.

3.0 Reaction Thermodynamics

Chemical reactions and their energy

A brief overview of the Aluminum/water/hydrogen chemistry and thermodynamics is given here. More details can be found elsewhere [2].

For the concepts described herein, aluminum is not used directly as a fuel, but rather creates hydrogen fuel from water reacted with aluminum. The water-to-hydrogen reaction is driven by the electrochemical potential of aluminum (near 3 Volts vs a hydrogen electrode) – but unlike in conventional electrolysis which produces H_2 and O_2 from H_2O, the H_2O reacts with the aluminum to form hydrogen and aluminum oxides and oxy-hydroxides. Water splits at around 1.5 V. Aluminum has a potential of 3 V, about 50% of the energy in the aluminum goes to forming H_2 (1.5 V reaction), and then other half forms low-grade heat (Q) that cannot be used effectively to make electricity. The following are possible reactions of aluminum with water to produce hydrogen:

$$2Al_{(s)} + 6H_2O_{(l)} = 2Al(OH)_{3\,(aq)} + 3H_{2\,(g)} + Q \text{ - (bayerite)} \quad 3.7 \text{ wt\% H2} \quad (1)$$

$$2Al + 4H_2O_{(l)} = 2AlO(OH)_{(aq)} + 3H_{2\,(g)} + Q \text{ - (boehmite)} \quad 4.8 \text{ wt\% } H_2 \quad (2)$$

$$2Al + 3H_2O_{(l)} = Al_2O_{3\,(aq)} + 3H_{2\,(g)} + Q \text{ - (alumina)} \quad 5.6 \text{ wt\% } H_2 \quad (3)$$

By comparison, the reaction for hydrogen production from water electrolysis is simply:

$$\text{electricity} + H_2O_{(l)} = \tfrac{1}{2}\, O_2 + H_2 + Q \quad (4)$$

Pure aluminum is corrosion resistant because it is protected by a naturally occurring thin aluminum oxide (Al_2O_3) layer, which forms almost immediately on the bare surface in air, as shown schematically in Figure 2. The key to efficient generation of the hydrogen producing reactions in Eqs. 1-3, is to disrupt or bypass this oxide layer so that all the aluminum in the reactant power can be utilized. A number of methods have been studied to accomplish this, including, but not limited to:

1) Immersing the aluminum in alkaline and acidic solutions to disrupt/breakdown the oxide layer.
2) Activating the aluminum by mechanical treatment of the metal using cutting or ball milling to various particle sizes to expose a fresh reactive surface. Then using this pure aluminum powder, or mixing it with additives such as salts or metal oxides to further disrupt the oxide layer.
3) Alloying the aluminum with liquid metals that naturally breakdown the oxide layer. These alloys use elements such as gallium (Ga), indium (In), zinc (Zn), tin (Sn), and are typically combined in a binary or ternary formulation. This alloying can be accomplished through molten casting, ball milling, and surface treatment diffusion. (see section 4.0 of this paper)

Reactions 1-3 all produce 3 moles of hydrogen gas per 2 moles of aluminum. However, the water consumption of the 3 reactions is different. Eq. 3, with alumina (Al_2O_3) as the product, is most desirable because only 3 moles of water are needed to produce the 3 moles of H_2. For this reaction, 54 grams (2 moles) of aluminum combined with 54 grams of water (3 moles) yields 6 grams of H_2 (3 moles)and 1 mole (102 grams) of Al_2O_3, or 5.6 wt% H_2. 1 kg of H_2 has 142 MJ, or 39.4 kWh HHV, or 120 MJ/33.3 kWh LHV, so 6 grams of H_2 have 240 Wh (HHV) or 200 Wh (LHV). The next most favorable reaction is Eq. 2, which produces the Boehmite phase of AlOOH and consumes 4 moles of water for every 3 moles of H_2 produced. So 54 grams of aluminum combined with 72 grams of water yields 6 grams of H_2 and 118 grams of AlO(OH), or 4.8 weight % H_2. If the water can be harvested, the H_2 is 11% of the materials weight of the reaction products (3 moles of H_2 produced from every 2 moles of aluminum). However, if the final weight of the system is relevant, the weight percent of H_2 is unchanged from Eqs 1-3, even if the water is harvested.

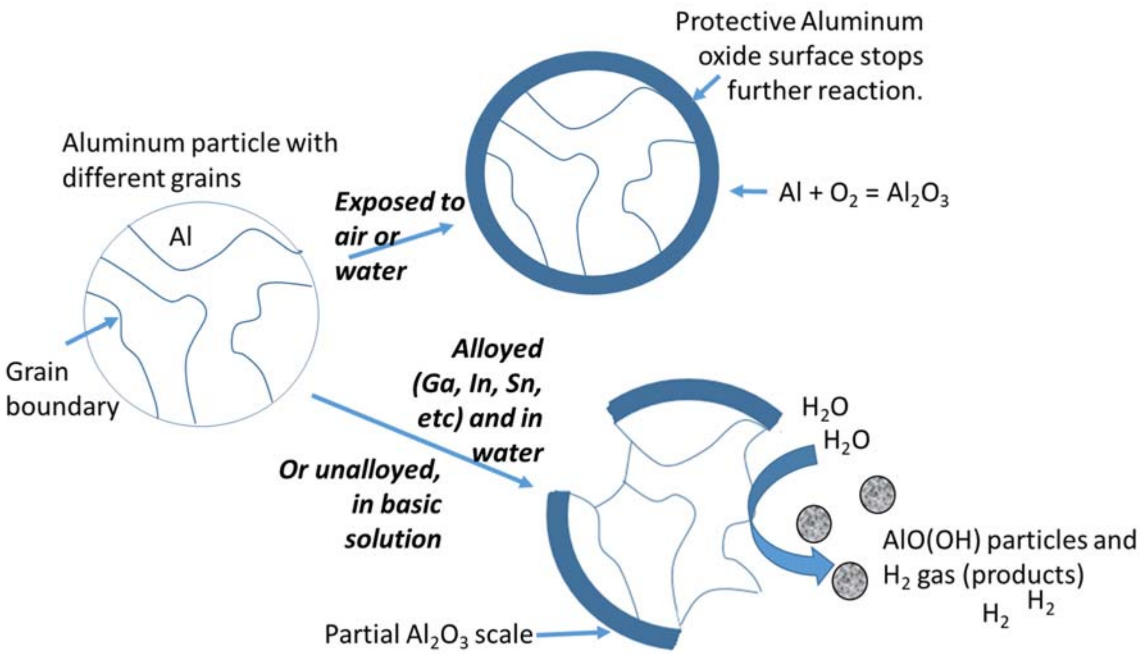


Figure 1. Schematic of mechanisms for aluminum particle interaction with the environment. Left – schematic of aluminum particle, with numerous grains. Right top – particle becomes covered in a protective Al_2O_3 scale. Bottom right – when the aluminum particles are either reacted in acid/base to remove the Al_2O_3 coating, or alloyed with Ga, In, Sn, etc, and the aluminum reacts with the solution to form H_2 and an aluminum oxyhydroxide. The reactions likely propagate along the grains in the metal.

The reactions that occurs in practice are dependent on the temperature and pressure of the reaction, which are highly dependent on the reactor design and operation. A summary of the general temperature and pressure conditions for aluminum/water reactions are shown in Table 1 below. The energy produced from the aluminum/water reactions in Eq. 1-3 are similar – nearly 900 kJ/mol. The volumetric energy density is reported to be between 83 - 85 MJ/L, or two times that of diesel fuel, and eight times that of liquid hydrogen. However, this is misleading because the 83 - 85 MJ/L of energy is for the full reaction of Aluminum with water to form aluminum oxygen byproducts, hydrogen, and heat. But only the hydrogen product can be used to make electricity. The heat produced by equations 1-3 is too low in temperature for any meaningful work. Secondly, the reaction energy typically only considers the weight and moles of Aluminum, and not of the water that is needed for the reaction.

Aluminum is also not attractive on a volume basis when the reaction products in Eq 1-3 are considered. Figure 1 shows a volumetric and weight comparison of how aluminum/water advocates often show the high energy value of the reaction (near 84 MJ/L) [2,3] compared to our assessment for the hydrogen energy produced and then the results renormalized again for the weight/volume of water that must be added (near 10 MJ/L). When only the useful energy of the hydrogen produced from the aluminum-water reaction is considered, the volumetric energy density of aluminum is only slightly higher than diesel and JP-8 fuel, and less desirable on a mass density basis. If both the aluminum and water reactant are included, the volumetric density is less than liquid hydrogen, and significantly less on a mass basis. While the mass energy and volumetric energy of the lithium-ion battery appears relatively low on the chart, the batteries come as nearly complete systems, and do not require energy conversion devices such as a fuel cell or generator.

Equation	T [°C]	P [mPA]	DG [kJ/mol]	Expected byproduct	Actual Byproduct(s)
1	0.1	6.9	-887	$Al(OH)_3$	$Al + Al(OH)_3$
1	4	6.9	-887	$Al(OH)_3$	$Al(OH)_3$
2	100	0.1	-887	AlO(OH)	AlO(OH)
2	230	6.9	-887	AlO(OH)	AlO(OH)

Table 1: Byproduct Model Validation Test Cases for Aluminum Reacted with Water, adapted from Godart et al. [2]

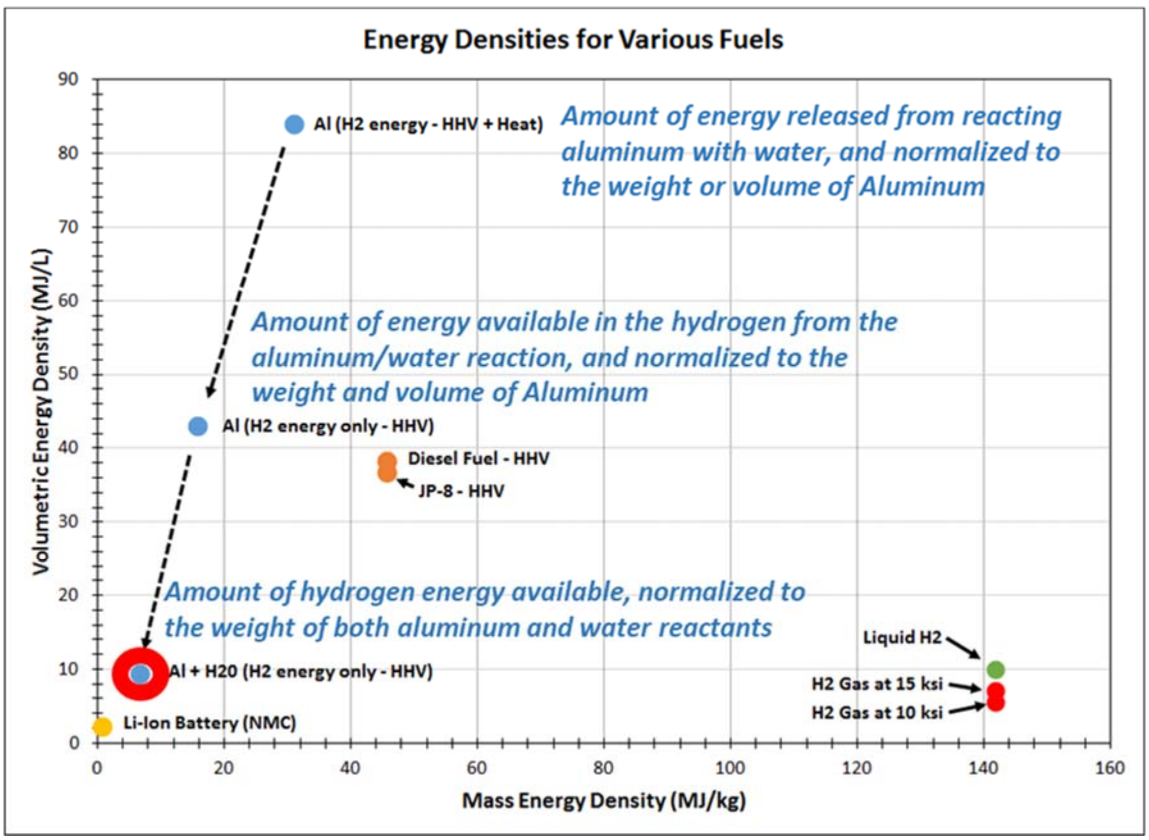


Figure 2: Energy Densities for the Aluminum-Water Reaction Compared to Other Fuel/Energy Sources. Aluminum is often advertised to have high energy density [E. Morgan, 2019 and Godard, 2019], but it is more accurate to consider the energy available in the hydrogen produced from the Aluminum-Water reaction, and where water cannot be scavenged, the water must be considered in the weight of the reactants (see Eqs 1-3).

In summary, the amount of useable energy (hydrogen) from the aluminum/water reaction is not compelling compared to diesel fuel and hydrogen, and technologists should be cautious to overstate the available energy of Aluminum/water reactions.

4.0 Aluminum Alloy Fuels

Numerous studies have shown that Al can be alloyed with varying amounts of gallium, indium, and tin [4-8]. Elitzur et al., demonstrated promising hydrogen production rates and yields with aluminum particles defused with a 1-2.5 wt% lithium activator [9]. Results are presented for various H_2O/Al mass ratios and different water types, including seawater, as well as slightly elevated water temperatures. Results are also presented for a closed reactor vessel initially at 1 atm pressure. Their paper describes a novel method of creating the lithium diffusion, but does not elaborate on any production method.

For this report, we focus on aluminum fuels based on aluminum alloys using liquid metals. These appear to demonstrate the highest production rates and yields, and are relatively safe to handle with minimal personal protective equipment (PPE). They also eliminate the need for corrosive solutions. Although gallium and indium are expensive metals, they can be relatively cost effective if used in small amounts to produce this aluminum alloy, even if the waste products are not recycled.

Table 2 contains a summary of recent studies on hydrogen generation performance from the reaction of aluminum alloys with water in a laboratory test case environment.

Metal/ Metal Alloy	Treatment Process	Sample Config.	H_2 Gen. Rate (gH_2/min/g Al)	Max. H_2 Yield (%)	Water Types	Op. Cond. (atm/°C)	Ref.
50 wt% Al, 34 wt% Ga, 11 wt% In, 5 wt% Sn	Molten casting at 700°C	80mg cleaved pieces	~0.04	83.3	Distilled	1 atm/ 45-55°C	4
97 wt% Al, Ga-In-Sn-Zn (50:30:10:10)	Ball Milling	<250 µm particles	~0.264 at 60 °C	~80-85, < 2 min	NA	1 atm/ 20-60 °C	5
89 wt% Al, 3 wt% Ga, 3 wt% In, 5 wt% Sn	Ball Milling	NA	~0.129, Distilled, Deionized H2O ~0.0824 Tap water	~99.2 in 3 min, with Tap water	Tap, Deionized Distilled	1 atm/ room temp.	6
96.5 wt% Al, 3-4 wt% Ga-In	Surface Treatment Diffusion	6mm sphere/0.3g Al	NA	90-97	5ml 18.2 MΩ Deionized	1 atm/ room temp.	7
88.1 wt% Al, 11.9 wt% Sn	Low Temp. Ball Milling	50-100 µm particles	As high as 0.165	100 in 5 min	Various, including Urine	1 atm/ 25°C	8
97.5 wt% Al, 2.5 wt% Lithium Activator	NA	9 µm particles/20 µm flakes	~0.05	90	Tap, seawater, distilled	1 atm/ 23-70 °C	9

Table 2: Recent Studies on Hydrogen Generation Performance from Aluminum Alloys

In many of the reaction experiments sited in literature, the hydrogen production rate can be dramatically increased (exponentially) by increasing the initial water temperature. In a reactor, this occurs once the temperature at the local reaction site increases to ~50 °C. This higher temperature also improves the % yield. There is very limited data on the impact (% yield, hydrogen production rate) for grey water or salt water. However, a number of researchers have claimed that their fuel will also perform under these conditions as well. This is a critical area for further research testing to quantify the impact of water quality on the reaction, and the resulting hydrogen product purity. Any unreacted aluminum is another penalty from the theoretical energy values of the aluminum/water reaction in Eqns 1-3 and Table 1.

5.0 Reactor Design Considerations

As discussed above, the aluminum and water are reacted to create hydrogen, which can then be used to make electricity in an energy conversion device like a fuel cell or combustion engine. This additional reaction is a key difference when comparing the aluminum/water technology against other fuels like JP-8 and hydrogen, which can be converted to useful power in their native state. One benefit of the extra conversion step is that none of the stored materials (aluminum alloys and water) are flammable by themselves. However, a Al/H_2O reactor is the cornerstone of any useful system.

The most prevalent reactor design seen in application use is referred to as a “bulk fuel” or “water limiting, pressure controlled” reactor. This type of a reactor is a closed volume unit that contains all the aluminum alloy fuel required to produce the intended hydrogen mass, as well as the byproduct that is formed as the aluminum alloy fuel is consumed. Water is injected in a limited fashion to control the desired internal hydrogen pressure. Therefore, a small mass of hydrogen is stored in the reactor chamber at all times. This provides an on-demand capacity for the energy conversion device. As hydrogen is consumed, the reactor pressure will decrease resulting in more water being injected to maintain the desired reactor pressure.

There are numerous examples of aluminum reactors in the literature. One example is given in Figure 3, for a reactor that produces hydrogen from using pure aluminum with an alkaline water solution. A similar design can be envisioned for aluminum alloys with a neutral water source.

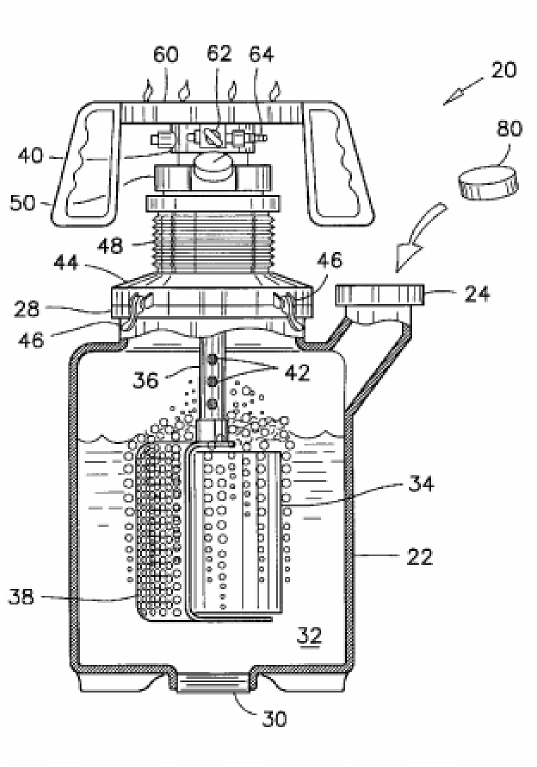


Figure 3. Reaction vessel for hydrogen production from aluminum water and sodium hydroxide, from reference [10]. In the figure, 80 is a pellet with small aluminum particles, through a fill opening (24), into a fuel cartridge (34) in a vessel (22), that is filled with water (32). The aluminum oxide/hydroxide product is cleaned out through the bottom (30); More details can be found in the patent.

Other reactor designs are possible, and should be further explored to identify their potential system advantages (i.e. actual water consumption, packaging volume/mass, other). However, for this analysis we will assume a “bulk fuel” water-limiting reactor based on its common use. Unless otherwise stated, the analysis will also assume a minimum reactor control pressure of 300 psia in order to target a lower ideal reaction water consumption. This also offers the advantage of a hydrogen supply pressure that more closely matches what is typically required by commercial fuel cell systems (95-135 psia) in the 5-30 kW range.

5.1 Reactor Internal Volume

A number of researchers stress the importance of ensuring that there is sufficient free space available in the reactor to allow for byproduct growth and proper reaction operation. In a closed reactor, if not enough free volume is present then the compaction of the byproduct can interact with the aluminum alloy fuel and stifle the reaction, or produce additional pressure on the reactor walls which could lead to reactor failure. Excess volume also makes it easier to clean the reactor after use, as the byproduct is less compact (the consistency of mud, versus cement). Managing byproduct density is critical, as this extra internal volume will have a significant impact on reactor packaging mass and volume.

The above requirement is focused on a closed volume “bulk fuel” reactor. Other reactor designs may minimize this required volume, such as a reactor that pumps/removes the byproduct during operation.

5.2 Reactor Vessel Mass and Size

Reactor material selection will be critical to the overall system mass and size. Table 3 contains our rough estimate of the mass and external volume for a "bulk fuel" water-limiting reactor that could produce a total of 2 kg hydrogen gas (~22 kg of Al fuel). The control pressure is assumed to be between 300-500 psia in order to target the boehmite based reaction equation (equation 2).

Reactor Vessel Material	Reactor Mass (kg)	Reactor Mass with Al Fuel (kg)	Reactor External Volume (L)
304 Stainless Steel	103.9	125.9	73.8
Titanium (Ti 265-12)	32.4	54.4	69.5
Stainless Steel COPV	10.7	38.0	55.3

Table 3: 1.75 kg Hydrogen Reactor Mass and External Volume for Various Build Materials (COPV = carbon overwrapped pressure vessel).

As seen from the table, material selection for the reactor will be key to maintaining an acceptable overall system mass and size. A smaller scale reactor operating close to ambient pressure (~20 psia) can offer a considerable reduction in mass and volume. However, this system would require more water (an ideal 50% increase going from the AlOOH to the $Al(OH)_3$ reaction) for the same hydrogen production.

5.3 Hydrogen Generation System (HGS) Balance of Plant (BOP)

An estimation of the balance of plant (BOP) required for a typical "bulk fuel" water limiting, pressure controlled reactor system can be found in Table 4. This BOP assumes a closed reactor system designed to control the boehmite based reaction (equation 2) at a pressure of at least 300 psia to minimize water requirements.

For very small hydrogen generation, a simple mechanically controlled reactor system designed to operate at pressures on the order of 20 psia would require much less BOP. However, this would require more water for the hydrogen generation reaction. Based on the table below, the components that could be eliminated in such a system would be: Heat Exchange/Fan, Water Pumps, High Pressure Water Pump, Pressurized Water Accumulator, and Sensor/Actuators.

Component	Comments
Reactor Vessel	Stores the aluminum alloy fuel and produces and stores hydrogen gas from the reaction. Minimum volume must be at least 3 times greater than the un-reacted packing volume required by the aluminum alloy.
Hydrogen Purification	Depending on fuel cell supplier requirements. Likely at least a water knock-out unit required to purify hydrogen gas.
Heat Exchanger/Fan	Provides cooling of the hydrogen gas for the water knock-out. May also be required for reactor cooling.
Water Pumps	Transfers accumulated water in knock-out back to water tank. Water pump for reactor cooling if required
Water Storage Tank	Stores reactant water at nominal temperature and pressure.
High Pressure Water Pump	Required to pressurize water accumulator.
Pressurized Water Accumulator	Stores pressurized water for reactor water injection.
Thermostat Controlled Water Tank Pad Heaters	If operation is planned in climates below 0°C
Sensors/Actuators	Water pressure sensor, reactor water flow controller/valve, water flow meter, reactor pressure sensor, reactor hydrogen shut-off valve, cooling system temperature sensors, cooling flow bypass valve.
Reactor Management Controller	To control hydrogen generation and maintain system operation safety.
Hydrogen Safety System	Only if system enclosure hydrogen gas capacity is >2.5 kg, then per NFPA-2, section 7.1.23 for Hydrogen Equipment Enclosures (HEE).

Table 4: Potential Hydrogen Generation System BOP List

5.4 HGS Hydrogen Gravimetric and Volumetric Capacity Estimates

Table 5 contains an estimation of the HGS hydrogen gravimetric and volumetric capacity based on the "bulk fuel" water limiting reactor system content outlined in Table 4. Results are present for the following 4 cases:

1) Containing both water and aluminum alloy fuel stored on-board, and no recover of water possible with the fuel cell system.
2) Containing both water and aluminum alloy fuel stored on-board, and a 90% recovery factor for water from the fuel cell system.
3) Containing only aluminum alloy fuel stored on-board.
4) Case #1 with a realistic assumptions for water consumption (2x over mass stoichiometry) and a 90% hydrogen yield.

This analysis is based on the following key assumptions:

- 90 wt% aluminum alloy fuel, ideal hydrogen yield, and ideal water consumption, except for case #4.
- No heat recovery work from the reaction.

- The reactor is operating at a minimum of 300 psia targeting the boehmite reaction equation (equation 2) Reactor material is type-3 carbon overwrapped pressure vessel (COPV), and water tank material is polyethylene plastic.
- An additional 5% is added to account for system BOP mass, and 2% for packaging volume.

Results for a typical type-3 COPV pressure vessel are also included in the table.

Case	HGS wt% H_2	HGS kg/L H2	Delivered Mass Energy Density - HHV (MJ/kg)	Delivered Vol. Energy Density - HHV (MJ/kg)
Both Aluminum Alloy fuel and Water, no Recovery	3.4	0.025	4.8	3.6
Both Aluminum Alloy fuel and Water, with Recovery	4.8	0.033	6.9	4.7
Only Aluminum Alloy Fuel	6.5	0.039	9.2	5.6
Case #1, with Realistic Assumptions for Water and Yield	2.2	0.018	3.1	2.5
350 bar Type-3 Pressure Vessel	5.2	0.017	7.4	2.4

Table 5: Estimated HGS H_2 Gravimtric and Volumetric Capacity and Delivered Energy Densities

The table results highlight the need to understand the system application to assess the actual energy densities possible with the aluminum alloy-water technology.

A smaller scale reactor operating close to ambient pressure (~20 psia) would change these results. There would be opportunity to reduce reactor mass and size. But this system would require more water (~50% increase based on the ideal reactions) for the same hydrogen production.

As a reference, the DOE 2020 targets for a Light-Duty Fuel Cell Vehicle (FCV) with a 10 ksi hydrogen storage system have a gravimetric capacity of 4.5 wt% and a volumetric capacity of 0.030 kg/L. Published data for the 2019 Toyota Mirai states that their hydrogen tank only (Type 4, carbon fiber-reinforced plastic over plastic liner) is meeting a combined gravimetric capacity of 5.7 wt%, and an estimated volumetric capacity of ~0.034 kg/L.

6.0 System Operation Analysis

6.1 Expeditionary Advanced Base Operations (EABOs) Study Cases

As part of this technology assessment, two example cases were evaluated using an aluminum alloy-water reactor to generate the necessary hydrogen to perform the following key tasks for a USMC Expeditionary Advanced Base Operation:

1) Provide hydrogen for a maximum of 5 kW AC medium mobile power generation using a PEM based fuel cell Gen-set for base operations for 7 days. The average AC energy delivery profile is 53 kWh/day.
2) Provide small scale bulk hydrogen gas generation and dispensing for fueling small PEM based UAVs, or lift gas for small communication balloons.
   a) Ability to refill 3x PEM fuel cell UAV applications per day, for 7 days. Each refueling event requires 176 g of hydrogen gas at 410 bar. This task assumes an outside power source capable of 2.25 kW continuous power delivery to perform the required gas compression. The total compressor AC energy required is 19.5 kWh.
   b) Provide hydrogen lift gas necessary to fill 3x communication balloons over a 7 day period. Each balloon requires 2.27 kg of hydrogen delivered at 200 psia

A diagram of the system content to perform these tasks can be found in Figure 4. Each of the above cases have been evaluated individually to assess the amount of aluminum alloy fuel and water required. The reactor is assumed to be a pressure controlled, water limiting design with a minimum operating pressure of 300 psia. Therefore it is targeted to produce the boehmite reaction equation (equation 2), and thus, reduce the required water amount. The aluminum alloy fuel is assumed to be 90 wt% Al, with a density of 2880 g/L (1-3 mm beads). A loose packing factor of 0.6 is used to estimate the fuel volume for transport logistics. The reactor is assumed to produce hydrogen at a 90% yield, and operate at the stoichiometric ratio for water. This stoichiometric assumption is optimistic and thus favorable to the aluminum alloy-water case. The reactor design choice may also play a part on the amount of water required. No assumptions are made regarding water quality. Therefore, it is assumed grey water or other water types will work equally well as distilled or de-ionized water for both the reaction and the necessary hydrogen purity. This needs to be proven with more fundamental research testing.

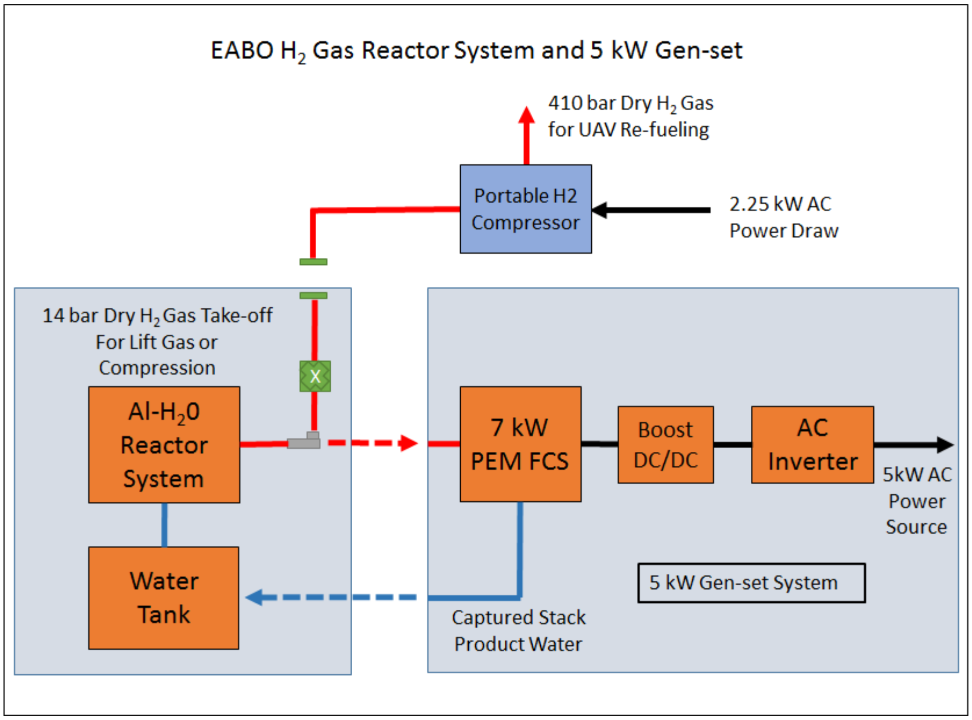


Figure 4: EABO Hydrogen Generation System and 5 kW Gen-set Example

An initial analysis for a fuel cell based 5 kW Gen-set, running only an average AC energy profile of 53 kWh/day over a 7 day period (case #1) can be found in Table 6. For this case, water is assumed to be captured from the fuel cell system at a recovery performance of 90%. The AC power generation efficiency of the fuel cell system is assumed to be 46% (LHV).

Mission Operating Duration (hrs)	Avg. Use Profile AC Pwr (kW)	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
168	2.2	24.2	0.90	266.6	154.3	104.7	105.0

Table 6: 5 kW Gen-set for 53 kWh/day AC power Delivery for 7 Days

As way of comparison, delivery of the same average AC energy profile in case #1 using a 5 kW Advanced Medium Mobile Power Source (AMMPS) generator would only require 158 kg of JP-8 fuel or 196 L. The 5 kW AMMPS generator is operating at an average efficiency ~20% (LHV) for this 53 kWh/day load profile.

An initial analysis for the UAV refueling case only (case #2a) can be found in Table 7.

Number of Tier2 UAV Fueling Events	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
21	3.7	0.90	40.8	23.6	44.1	44.2

Table 7: Case #2a, 3 UAV Refueling events/day for 7 Days

This task could potentially be achieved using a controlled reactor at higher pressures that could reduce, or even eliminate the need for the previously mentioned auxiliary compression system. This is a system design option that could be explored as it could reduce or eliminate the power, cost, footprint, and maintenance of an auxiliary compression unit.

Results for the communications balloon lift gas case (case #2b) can be found in Table 8.

Number of Balloon Fueling Events	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
3	6.81	0.90	75.0	43.4	81.1	81.4

Table 8: Case #2b 3 Communication Balloon Fueling Events over the 7 Day Mission

This task could potentially be achieved using a simple low pressure, mechanically controlled "bulk fuel" reactor requiring only 25 kg of aluminum alloy fuel for each balloon filling event.

Note, for these small scale bulk hydrogen gas generation and dispensing cases (2a, 2b), it would be possible to employ multiple units to support higher hydrogen demand in an EABO setting when necessary.

6.2 Small Portable Power Recharging

Small portable power recharging was another case evaluated for the aluminum alloy-water hydrogen generation technology. The analysis was focused on an aluminum alloy-water hydrogen generation system coupled with a PEM based fuel cell unit that could produce 30 W of power and 1200 Wh in support of dismounted squad level battery re-charging. For this analysis, the fuel is assumed to be the Al slurry described in section 4.2 at 86.4 wt% Al, as this form factor may offer advantages for transport logistics and refueling. The hydrogen generation system utilizes a conceptual stainless steel reactor. The reactor is sized to contain all the aluminum alloy fuel necessary for the 1200 Wh energy delivery. The reactor is mechanically controlled at a pressure of ~20 psia, and the reaction byproduct is assumed to be bayerite (equation 1). To minimize overall unit footprint, the water tank is sized for only 8 hrs of operation. Therefore, the water tank needs to be re-filled 4 times to complete the 1200 Wh energy delivery.

The reactor yield is assumed to be 90% at an over stoichiometric mass ratio of 2 (H_2O/Al). The AC power generation efficiency of the fuel cell system is assumed to be 40% (LHV)

In order to calculate overall unit energy densities, the fuel cell system and unit BOP were estimated based on previous work done by MIT, MIT-LL to design an Emergency Power Pack (EPP) for the USMC.[11] Although only an estimate, this design was well optimized for packaging the fuel cell system, power electronics and reactor control hardware.

As with the previous analysis cases, no assumptions are made regarding water quality. Therefore, it is assumed grey water or other water types will work equally well as distilled or de-ionized water for both the reaction and the necessary hydrogen purity. This needs to be proven with more fundamental research testing. A summary of the above assumptions can be found in Table 9.

Item	Description
Al Fuel Configuration	MIT Slurry, 86.4 wt% Al, Density: 2218 g/L
Reactor Control Pressure	40 psia, Bayerite reaction
Water Consumption	2 x reaction equation mass ratio (H2O/Al)
Expected Reactor Yield	90%
AC Power Efficiency (LHV)	40%
Fuel Cell System and Unit BOP Mass/Volume	433 g / 555 cm^3

Table 9: Assumptions for 30 W, 300 Wh Portable Power Charger Analysis. The system reaction analysis results for this application can be found in Table 10.

Mission Operating Duration (hrs)	Avg. Use Profile AC Pwr (kW)	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Mass Over Stoich Factor (H2O/Al)	Carried Water Required (kg)	Carried Water Required (L)
40	0.03	0.09	0.90	1.04	2.0	3.2	3.2

Table 10: 30 W, 300 Wh Portable Power Charger

An estimation of the HGS hydrogen gravimetric and volumetric capacity for this application case can be found in Table 11. Results are presented with and without carried water. The without water case represent a scenario where it is assumed water can be scavenged in field. Also included is the expected gravimetric and volumetric capacity for using type-3 compressed hydrogen canisters at 350 bar. These canisters have a 2x safety factor on pressure. Note from the table, even if the required water is not included in the analysis, compressed gas canisters could offer an advantage for at least total unit mass. It may also offer advantages regarding refueling complexity of the unit in the field.

HGS Grav. Capacity w/water (wt%)	HGS Vol. Capacity w/water (kg/L)	HGS Grav. Capacity w/o water (wt%)	HGS Vol. Capacity w/o water (kg/L)		Type 3 H2 Tank at 350 bar (wt%)	Type 3 H2 Tank at 350 bar (kg/L)
1.7	0.015	4.4	0.034		5.2	0.017

Table 11: HGS Gravimetric and Volumetric Capacity Compared to 350 bar Type-3 H_2 Compression

Similar types of fuel cell based portable power systems are already available in the market place. Examples include: UltraCell-XX55, and SFC Energy-Jenny600S/1200. The UltraCell product uses a reformed methanol fuel cell, while the SFC product uses a direct methanol fuel cell. Both systems use refillable or replaceable methanol based fuel cartridges. These products are only provided as examples for benchmarking, and are not an endorsement by the authors of their real world capabilities.

Contained in Figure 5 is a graph showing the delivered energy densities of the aluminum alloy-water based small portable power charging system versus some other competing alternatives. Also included is the compressed gas option mentioned earlier, and a Li based charger that the authors feel represents the current market "best in class" for a battery based example.

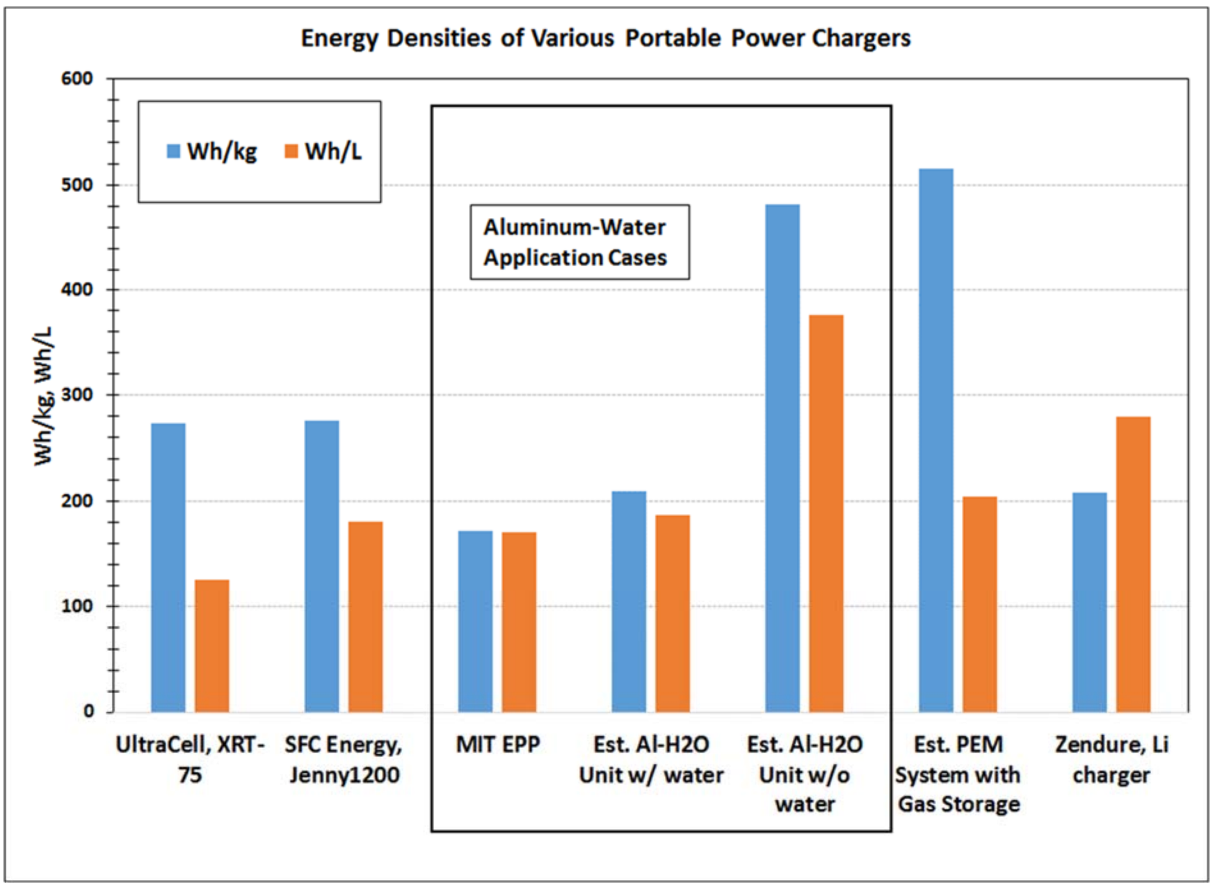


Figure 5: Energy Densities of Various Portable Power Chargers

As seen from the figure, the aluminum alloy-water based system has potential for competitive delivered energy densities, especially if an acceptable water source can be scavenged in the field. However, effort should be focused on a detailed design study to identify options for improving the overall HGS gravimetric and volumetric capacity.

7.0 Logistics Considerations

7.1 Fuel Transportation

Figure 6 shows the logistics footprint comparison for one week of 5 kW medium mobile power generation per the use case found in Table 6. The aluminum alloy fuel is assumed to be contained in a permeable bag to support ease of handing and reactor refueling. One 7 L ammo can (~12.7 kg aluminum alloy fuel) would represent 8 hrs of operation before refueling. 11 L (~ 19 kg) of fuel would be required for 12 hrs operation, which is comparable to the diesel/JP-8 generator refueling interval. It is assumed that a dedicated vehicle and/or trailer would be required for unit transport. Existing vehicles and trailers would support the weight (~825 lbs.) and volume of the aluminum alloy-water hydrogen generation system/PEM fuel cell Gen-set as it should be on par with comparable diesel/JP-8 units.

Power	Fuel	Duration	Logistics Footprint - Fuel
5 kW[1]	Al/H_2O Mix	7 Days (168 Hours)	  267 kg/154L 105 kg/105L **(22) 7L Ammo Cans and (7) 20L Water Cans**
	JP-8		 158 kg/196L **(10) 20L Fuel Cans**

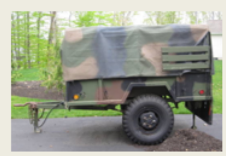
Power	Fuel	Duration	Logistics Footprint – Energy Conversion and Mobility
5 kW[1]	Al/H_2O Mix	7 Days (168 Hours)	  **(1) JLTV and (1) M101 Trailer mounted Al Reactor and Fuel Cell** Total load out = 754 kg/ 1,190L
	JP-8		  **(1) JLTV and (1) Trailer Mounted MEP-1030A Generator** Total load out = 513 kg/ 1,042L

Figure 6: Illustration of Logistics Footprint of Field Systems

In a head-to-head comparison with a JP-8 fueled generator, the JP-8 fuel has a smaller fueling logistical footprint with 158 kg of fuel required versus 267 kg of Al fuel and 105 kg of water (372 kg total) for the aluminum alloy-water hydrogen generation system based Gen-set for the same electrical energy delivery.

However, the USMC has identified bulk fuel logistics as a potential vulnerability. The aluminum alloy fuel solid form factor and paste form factor may provide commanders greater options for battlefield transport logistics. This includes the possibility of safely air dropping the fuel, or potentially scavenging and activating scrap aluminum. The potential value of these options needs to be quantified by the appropriate DOD logistics experts. It can then be determine if the corresponding research to further mature the production, packaging, and transport of these novel energy forms is warranted.

7.2 Estimated Aluminum Alloy Fuel Costs

A cost analysis of the aluminum fuel compared to JP-8 can be found in Table 12. The JP-8 results are based on data available from the Defense Logistics Agency (DLA) for FY2020 procurement standard fuel pricing (SFP). The aluminum fuel prices are generated from retail pricing for the base materials used to alloy the specific fuel (i.e. aluminum, gallium, and indium, tin), and does not include any processing or manufacturing cost estimates**. All the fuel costs, including JP-8, do not include any cost of logistics to transport the fuel to the point of use.**

For the recycled Al fuel, aluminum pricing is based on secondary aluminum (scrap), which is aluminum is ~1/3 the price of pure aluminum. Slocum has successfully recycled aluminum from scrap with a process that is based on surface treatment diffusion, and uses a binary mixture of gallium, and indium [7]. It appears to require only minimal investment to produce and could offer the USMC more flexibility regarding procurement options. This could also include the ability to produce the fuel closer to the tactical edge.

We compare this to a fuel with 90 wt% Al and a ternary mixture of gallium, indium, and tin using pure aluminum. There is some merit to using 1100 series aluminum with a low silicon amount to prevent the formation of silane (H_4Si) in the hydrogen gas production. Among the normal safety hazards associated with silane (pyrophoric gas), if the resulting hydrogen gas is used in a PEM based fuel cell system it can also poison the fuel cell membrane. Therefore, care must be taken regarding the Si content when using secondary/scrap aluminum.

In Table 12, the aluminum fuel cost analyses assume ideal (100%) reaction yield, and the LHV of the hydrogen produced. Energy conversion for the produced hydrogen is assumed to be 50% (hydrogen fuel cell), while the JP-8 is assumed to be 20% (a conservative assumption).

	JP-8	Al Fuel (recycled)	Al Fuel (pure)
wt% Al	NA	98%	90%
LHV (MJ/kg fuel)	42.8	13.17	12.10
Fuel Cost ($/kg)	$0.97	$6.98	$30.77
Energy Conv. Efficiency (LHV)	20%	50%	50%
Delivered $/MJ (after energy conversion)	$0.11	$1.06	$5.09
Production Process/Equipment Cost	NA	Low	Moderate - High

Table 12: Aluminum Alloy Fuel Cost Analysis

It can be assumed that recycled Al fuel is on the low end of the cost spectrum, and high purity fuel would be on the high end of the cost. As seen from the table, the recycled alloy fuel (material only) represents a factor of 9 greater cost than JP-8 on a delivered energy basis, and the pure aluminum alloy fuel represents a factor of 45 greater cost than JP-8 on a delivered energy basis.

7.3 Estimated Cost of Hydrogen Generation versus Electrolysis

Looking purely at the cost of hydrogen generation, Figure 7 contains a graph comparing aluminum alloy-water hydrogen generation to relatively mature and commercially available electrolysis based systems. The electrolysis system includes generation, compression, and dispensing of hydrogen at 350 or 700 bar for light duty vehicle applications. Total system efficiency (LHV) is assumed to be 45%, which is conservative considering the efficiencies of existing products on the market. The power needed for this system is assumed to be provided by a JP-8 generator operating at 20% LHV efficiency, also a conservative assumption.

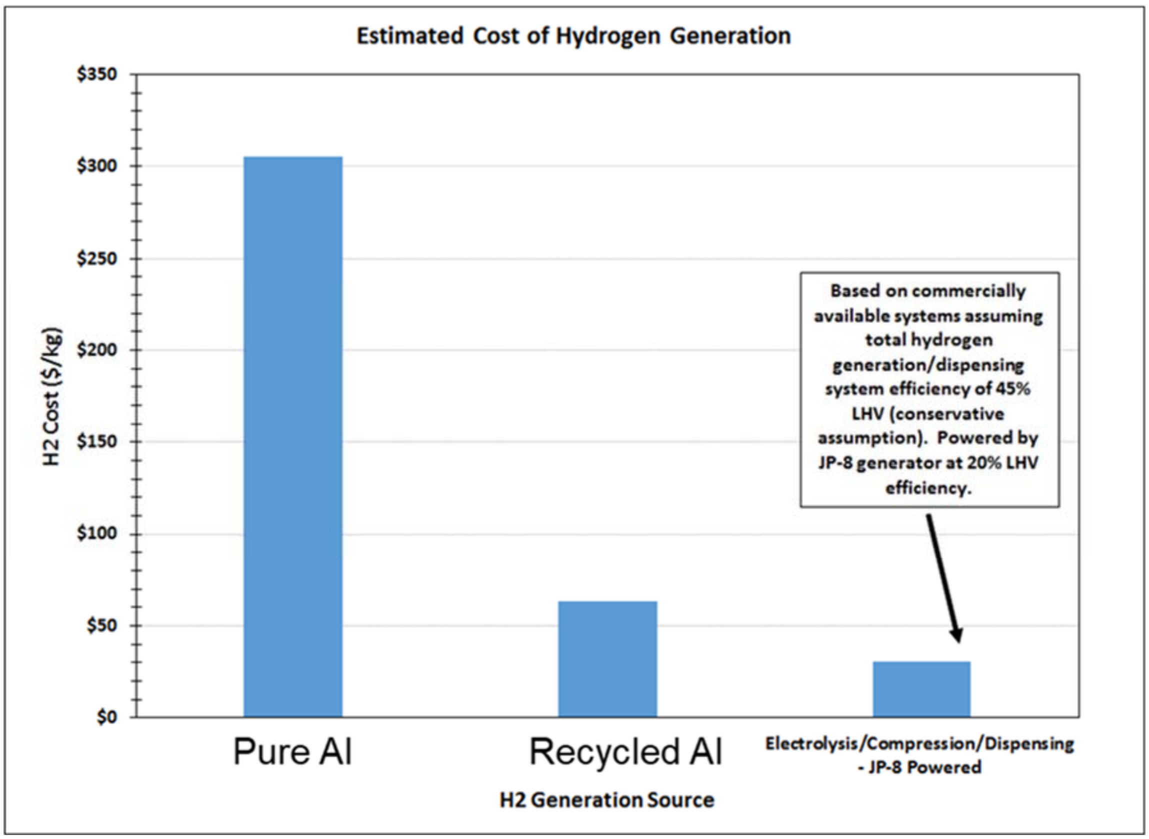


Figure 7: Estimation for the Cost of Hydrogen Generation – Aliminum-Water versus Electrolysis

As can be seen from the graph, the cost of hydrogen generation using aluminum alloy-water is at best at least twice the cost of using a conventional electrolysis system powered by a JP-8 generator. Note also, the aluminum alloy-water cases above only include the aluminum alloy fuel material cost and does not take into account any additional system losses/costs for compression if necessary, or fuel process manufacturing. **Neither the aluminum alloy-water nor electrolysis generated hydrogen cost takes into account the logistics to transport the fuel (JP-8 or Al Alloy), or necessary equipment to the point of use.**

7.4 Large Scale Hydrogen Generation

Figure 8 contains a graph showing the required power and JP-8 fuel necessary for electrolysis, versus the mass of aluminum alloy fuel necessary with aluminum-water, for bulk hydrogen production. This analysis assumes an electrolyzer/compression system efficiency of 50% (LHV) and power conversion using a JP-8 generator at 40% (LHV). The aluminum water calculations are based on the boehmite reaction (equation 2) with a fuel alloy at 90 wt% Al and a hydrogen yield of 95%.

Electrolysis is the most mature and commercially available technology for this task, and a more cost effective solution looking purely at the base fuel costs in Figure 7. However as seen from the graph, it would require a significant AC power source and JP-8 fuel to produce hydrogen in large quantities. At 30 kg/day production, the electrolysis system requires ~83 kW power and ~524 L/day of JP-8 fuel. The aluminum alloy-water system would require ~330 kg/day aluminum alloy fuel. Both approaches represent a significant transport logistics burden for fuel necessary to generate bulk hydrogen in large quantities.

Theoretically, electrolysis also requires 25% less water per kg of hydrogen produced then the ideal aluminum alloy-water reaction (equation 2), but requires water of a specific purity. In practice, there would likely be much more water needed for the aluminum alloy-water approach based on actual reactor water consumption requirements mentioned previously, and if the reactor design uses excess water for cooling (likely the simplest design approach).

In the case of large scale hydrogen generation for refueling, there is no apparent safety advantage for the aluminum alloy-water generation approach over electrolysis, as both systems would be required to store significant quantities of compressed hydrogen gas for dispensing.

Considering the above, a much more detailed comparative analysis is required between aluminum alloy-water and electrolysis before identifying the correct approach for larger scale hydrogen generation if, or when the USMC desires this for their future mission roadmap. This analysis should include the required optimized equipment footprint and transport, available supplier based, as well as the required fuel logistics and options (aluminum alloy versus. JP-8).

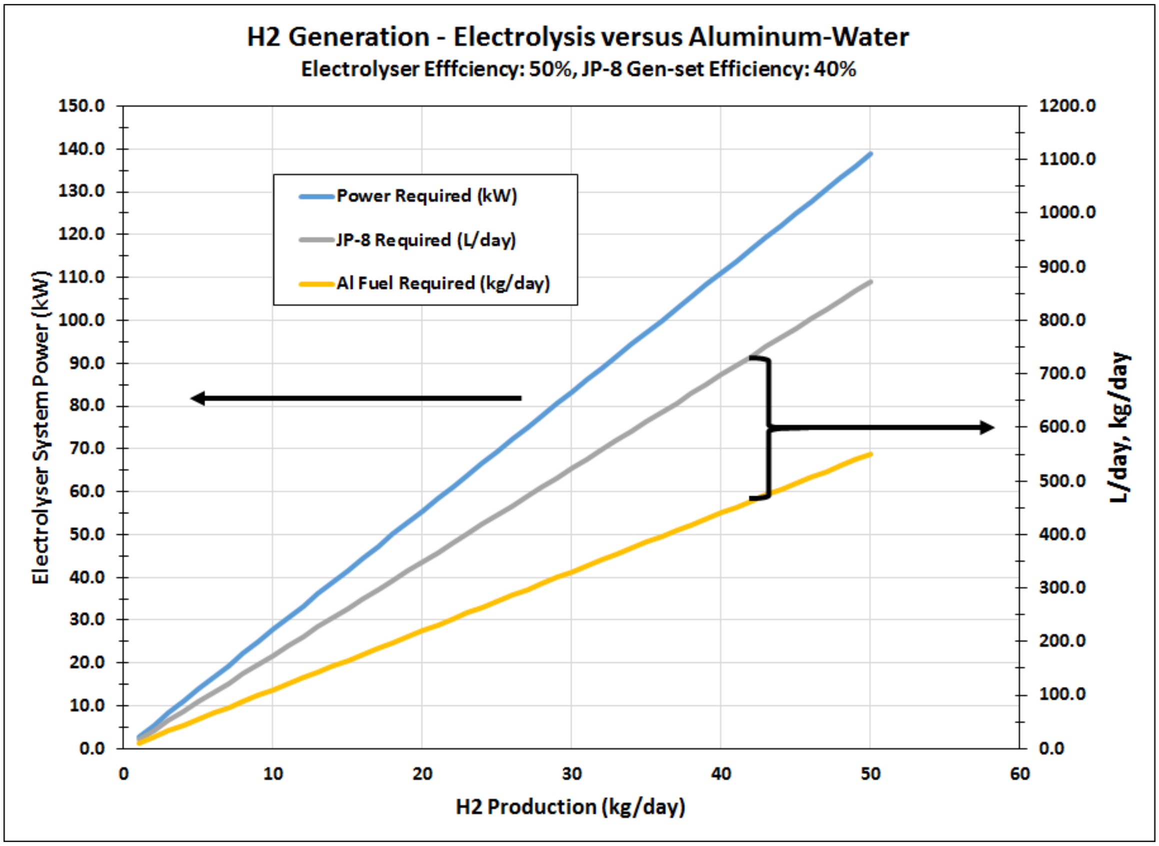


Figure 8: Hydrogen Generation Electrolysis versus Aluminum alloy- Water for Large Scale Hydrogen Production

8.0 Conclusions

First, it is important to reiterate that the aluminum alloy-water technology is a hydrogen generation system, and with the exception of lift gas, still requires an energy conversion device to do useful work. The most efficient energy conversion device to do this would be a PEM based fuel cell. **It is important that the USMC also considers the need for robust and durable fuel cell products, as well as supply sources when considering the application of this technology.**

Based on a review of previous work funded by the DOD, it is the authors' assessment that the aluminum alloy-water hydrogen generation system technology is at TRL 5-6, and a MRL of 3-4.

The technology assessment and case study examples presented in this report support the following conclusions for the application of aluminum alloy-water hydrogen generation as an energy source:

1) <u>Small Scale Standalone Hydrogen Generation/Dispensing (2-4 kg/day hydrogen)</u>

   The aluminum alloy-water hydrogen generation system does look favorable as a source of on demand gaseous hydrogen supply for small scale systems already operating on hydrogen as an energy source (small UAVs, group 2), or applications that require an effective lift gas (balloons). This assumes the necessary water source is available in the EABO/FOB setting. Advantages include:

   - Depending on reactor and system design, this system could reduce or eliminate the need for high quantities of a compressed flammable gas (hydrogen) at the point of use.
   - Eliminates the need to transport bulk compressed gas cylinders, and enables bulk storage and transport of safe to handle and non-flammable reactants (aluminum alloy and water) that require another processing step to make a usable fuel or lift gas (hydrogen).
   - Eliminates the need for significant power generation and JP-8 fuel that would be necessary to utilize more mature technology (electrolysis) for hydrogen generation.

2) <u>Small Portable Power Recharging (<0.1 kg/recharge)</u>

   Marine infantry squad small portable power recharging offers another potential application of this technology in the near term if no small scale hydrogen generation and dispensing is available in an EABO setting. A simple, compact, and light aluminum alloy-water hydrogen generation unit combined with a fuel cell based power delivery system could offer advantages for squad level patrol battery charging. This is especially true if no additional water is required to be carried, and the water necessary for the reactor/system can be scavenged in field. This type of unit could replace other power sources used for this effort that result in extra carried weight, or inefficient and high noise signature power conversion. Examples include: military vehicle APUs, extra batteries, or high capacity portable Li-Ion battery chargers.

   However, if small scale hydrogen generation and compression is already available in an EABO setting for other strategic purposes, then these small portable power recharging systems may be better served using a replaceable and refillable "cartridge type" compressed hydrogen gas canister to minimize the impact on overall unit weight and potentially volume. Infantry squads can then carry multiple cartridges (already full) depending on the expected mission use profile. Note, the mass and therefore the energy content of hydrogen is small in this system case and should represent little concern for safety in use.

A comprehensive system design study is warranted here to identify the maximum potential for gravimetric and volumetric capacity of the hydrogen generation system for such an application. This design effort should also be focused on simplifying the reactor refueling effort in the field. Then the resulting unit delivered energy densities (Wh/kg, Wh/L) from this work can be more accurately benchmarked against compressed gas hydrogen storage, or other similar types of fuel cell based portable power systems are already available in the market place.

3) Large Scale Standalone Hydrogen Generation/Dispensing (5-50 kg/day hydrogen)

Aluminum alloy-water can also offer a technically feasible path for large-scale hydrogen gas generation, storage, and dispensing if the USMC adopts additional mobile hydrogen applications such as hydrogen-electric UTVs or light duty fuel cell ground vehicles for tactical agility and reduced battlefield signature. This is also applicable to large balloon inflation applications. There is no question that light duty mobile ground vehicle systems are best served using compressed hydrogen on-board (at 350 or 700 bar) as the fuel storage method to minimize system complexity, weight, and packaging volume. In this respect, the authors agree with the original DOE 2010 assessment in reference 1. These applications then must be refueled with compressed gaseous hydrogen. The aluminum alloy-water hydrogen generation approach looks especially attractive where high quantities of hydrogen production are desired and an appropriate AC power source for an alternate technology like electrolysis (most mature) is not available in a forward deployed scenario. Assuming hydrogen generation is done at sufficiently high pressure, it also eliminates mechanical compression which should offer a benefit in equipment maintenance.

However, a much more detailed comparative analysis is required between aluminum alloy-water and electrolysis (and potentially other options) before identifying the correct approach for larger scale hydrogen generation if, or when the USMC desires this for their future mission roadmap. Considerations should include: required optimized equipment footprint and transport, technology maturity, available supplier based, and fuel logistics (aluminum alloy versus JP-8).

4) Medium Mobile Power Generation (~2 kg/refuel)

There is no advantage for the aluminum alloy-water hydrogen generation system as an energy source over diesel/JP-8 for stationary EABO 5 kW AC power generation. Based on the analysis provided, this would be the case for higher AC power deliveries as well, as theses diesel/JP-8 generators typically operate at even higher efficiencies. Although the total weight and volume of the hydrogen based Gen-set unit including the hydrogen generation system would be on par with a diesel/JP-8 unit (likely slightly lower), it does not offer any real advantage in the area of battlefield fuel logistics where an abundance of JP-8 is already available for other purposes (i.e. mobility). As seen from Table 6 and Figure 6, the mass of aluminum alloy fuel is 1.69 times the mass of the required JP-8 for the same power generation. Even if the reactor hydrogen yield is assumed ideal (100%), the mass of aluminum alloy fuel is still 1.5 times JP-8. On a volume basis, the packing volume of the aluminum alloy fuel is 0.79 of JP-8. Note however, that these mass and volume numbers do not yet include the additional water logistics that would be required for the hydrogen generation system to produce the necessary energy source.

The aluminum alloy-water hydrogen generation also adds significant system complexity to generate the energy source that is not present with a JP-8 generator system. Lastly, the AMMPS diesel/JP-8 generator is operating at only 20% efficiency on the load profile evaluated. This could be improved dramatically by simply adding mature battery hybrid technology to the existing IC engine generator system solution.

Utilization of the available heat energy is often cited as a key advantage of the aluminum alloy-water hydrogen generation reaction, however reactor design research in this area is only at a very early stage. For a "bulk fuel" water limiting reactor, the quality of this heat source for potential work is not substantially greater than what can also be captured with a diesel/JP-8 engine. Combined heat-and-power alternatives can also be explored with existing diesel/JP-8 generator technology.

5) Other Application Considerations

For applications that require a significant quantity of on-board and on demand hydrogen gas, the use of aluminum alloy-water generation can offer safety advantages. The safety advantages of the aluminum alloy-water system include:

- Only small amounts of energy in compressed hydrogen gas form is ever stored in the vessel energy section during operation.
- Elimination for the need to generate, store and or transport significant compressed hydrogen gas to execute system fueling.
- The ability for bulk storage and transport of safe to handle and non-flammable reactants needed to fuel the application.

Applications that do not require any on-board water storage also offer potential advantages for the aluminum alloy-water hydrogen storage system as well. Assuming no water storage, and an aluminum alloy alloy of 90 wt%, the ideal gravimetric hydrogen capacity from the reaction is 10.1 wt%. This enables the potential for an on-board aluminum alloy-water hydrogen generation system to exceed the gravimetric capacity of state of the art compressed hydrogen storage (5-5.5 wt% with 2x safety factor). Assuming no detrimental reaction performance and the necessary hydrogen purity with seawater, then examples of this type of application would include:

- Hydrogen fuel cell powered vessels where water is drawn from overboard to support the necessary hydrogen generation.
- Sea-floor (sub-sea) fuel cell based power systems where water can be supplied externally for hydrogen generation (although this does not solve the requirement for the oxygen needed to operate a fuel cell under water).

9.0 Recommendations

If the future USMC mission (technology) roadmap potentially includes hydrogen fuel cell power systems or hydrogen lift gas, then there would be benefit for further investigation of the aluminum alloy-water hydrogen generation technology in the following key areas:

1) Development and build of a scalable bench top water-limiting, pressure controlled reactor for fundamental operational testing/learnings that currently does not exist in the available research literature.
    - 1-2 L internal volume to support 500 -1000Wh, electric energy (assuming 40% efficiency fuel cell).
    - Internal heat exchanger for capability of reactor cooling.
    - Capable of pressures as high as ~350 bar.
    - Optimized water injection.

   This would offer a test platform for the following key learnings regarding the technology and its future application benefit:
    - A standard test bed to benchmark/quantify new lower cost fuel formulations/approaches – characterizing average reactor yield, production rate, **hydrogen purity.**
    - Validation/Refinement of thermodynamic modeling, and desired reactor operating conditions to achieve targeted reaction byproduct.
    - **Quantify actual water consumption**, and mechanisms affecting it. Provides knowledge for operating strategies and reactor design considerations to minimize water consumption.
    - Characterize impact and maximize byproduct compaction to reduce reactor size.
    - Quantify the reaction performance and **hydrogen purity for non-ideal water sources** (i.e. grey water, seawater, other).
    - Provides critical learnings, and knowledge base for reactor design simplification and optimization strategies.
    - Provides a platform to **develop and validate reactor control strategies**, as well as reactor state modeling.

2) Pursue near term system design and prototype demonstration on efficient, simple, and safe (on-demand) small scale hydrogen generation and dispensing for military applications that already require/desire hydrogen in the field (i.e. small UAVs, small balloon lift gas). Target system design concept to eliminate the need for secondary compression/power if possible, and optimize overall unit footprint and weight.

3) Pursue a comprehensive system design study to identify the maximum potential for delivered energy densities (Wh/kg, Wh/L) using an aluminum alloy-water hydrogen generation system for small portable power charging applications. Execute benchmarking against comparative alternative options before pursuing prototype build and test.

10. Acknowledgments

The authors would like to thank the Office of Naval Research for funding this work.

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Assessment of conceptual energy systems using hydrogen produced from the reaction of aluminum alloys with water

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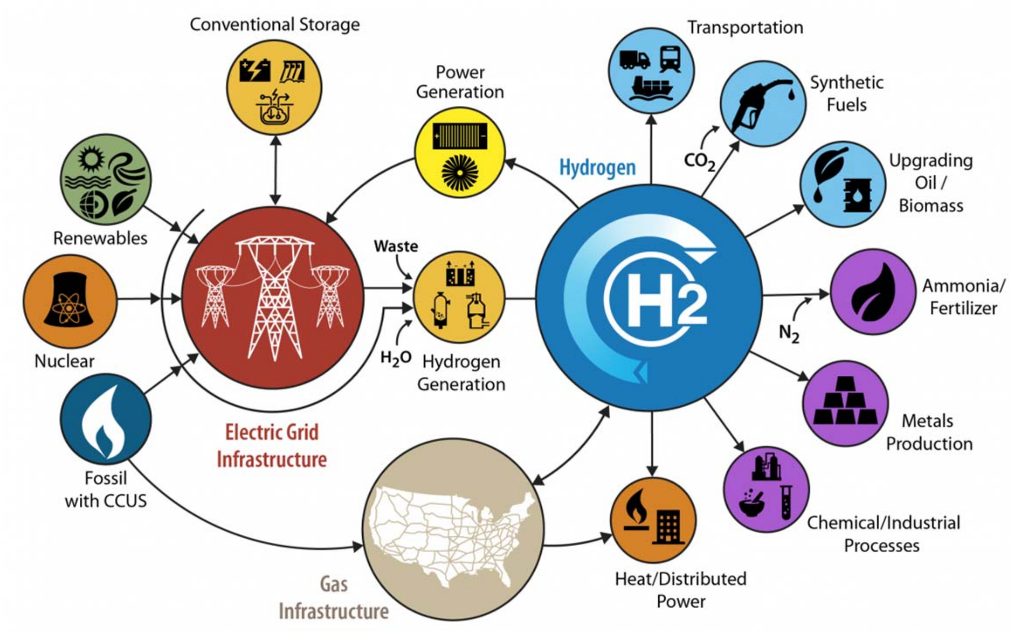
Edward Himes, EG Himes Consulting

Report to Dr. Joe Parker, Office of Naval Research Code 33
January 2021

A hydrogen economy??

DOE H2@Scale https://www.energy.gov/eere/fuelcells/h2scale



CLIMATE CHANGE

The Biden-Harris plan to create union jobs by tackling the climate crisis

https://buildbackbetter.gov/priorities/climate-change/

- **Innovation:** Drive dramatic cost reductions in critical clean energy technologies, including battery storage, negative emissions technologies, the next generation of building materials, renewable hydrogen, and advanced nuclear – and rapidly commercialize them, ensuring that those new technologies are made in America.

But the DOD/Navy is not ***GREEN*** – need mission effectiveness!!

The USMC Sees Hydrogen as Possible Solution to Forward Basing

DEPARTMENT OF THE NAVY
HEADQUARTERS UNITED STATES MARINE CORPS
3000 MARINE CORPS PENTAGON
WASHINGTON DC 20350-3000

IN REPLY REFER TO
3000
CMC

MAY 0 6 2019

MEMORANDUM

From: Commandant of the Marine Corps
To: Chief of Naval Research, Office of Naval Research

Subj: ESTABLISHMENT OF NEW INNOVATIVE NAVAL PROTOTYPE(S)

1. The need to develop and field leap-ahead capabilities has become apparent as the Marine Corps shifts from a capabilities-based approach to a threat-based approach in determining how it mans, trains, and equips the force. As such, investment in technology areas that have high operational impact and potentially game-changing effects to likely adversaries is necessary. I consider development of the below capabilities ultimately beneficial to both the Navy and Marine Corps and worthy of your organization's attention:

a. Unmanned Autonomou... concept of first and secon... Formalizing this concept i... continued development.

b. Hybrid Energy Mari... some types of energy such... technically tenable. Whi... is in aviation, the logist... ground vehicles could be s...

b. Hybrid Energy Marine Air Ground Task Force (MAGTF) - Hybridization of some types of energy such as electrical, hydrogen, and fuel cells is technically tenable. While the majority of heavy fuel consumed by the MAGTF is in aviation, the logistical burden of moving fuel on the battlefield for ground vehicles could be significantly reduced with hybridization.

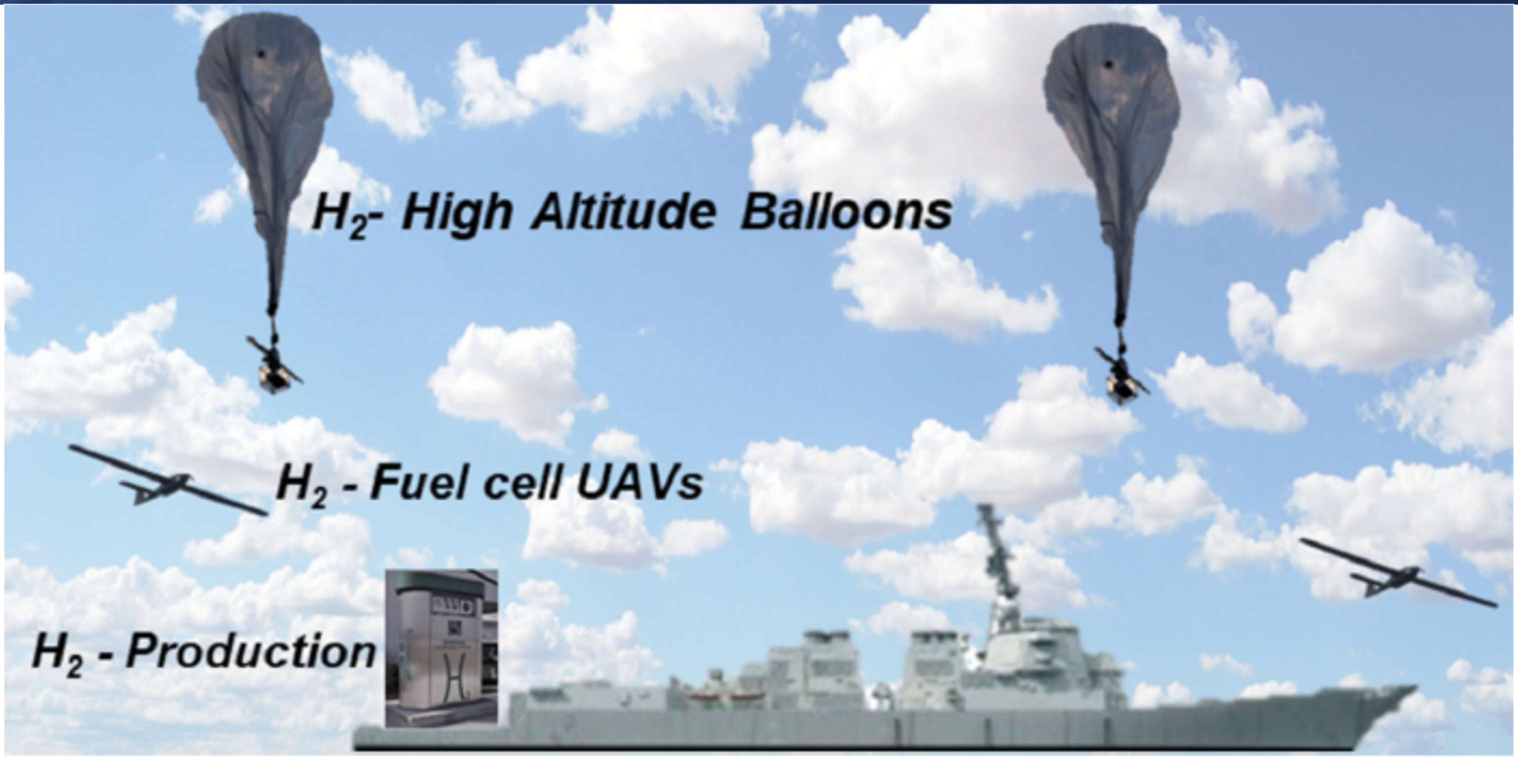
c. Fast, Long Range Connector - Engineering analysis supports the technical plausibility of a connector that could travel 40+kts with a 1000 mile range and 60,000 lb payload. Such a capability would more easily enable ship to shore movement of Marines and equipment in an anti-access/aerial denial environment.

d. Strategic Management Support Tool - This capability would integrate information horizontally and vertically within the MAGTF, provide only relevant information to decision makers, assist in the decision making process, and increase operational tempo. This capability is currently an unfunded Deliberate-Universal Needs Statement I signed on 23 Oct 2015.

2. I welcome a discussion on how the Office of Naval Research could establish new INPs to make these, or other capabilities, a reality to help us achieve our mutual objectives. I look forward to meeting with you soon.

Robert B. Neller

Example: Operational use of hydrogen



Use for hydrogen balloons for comms relays

In hydrogen UAVs.

Concern about safety

Hydrogen typically made by electrolysis

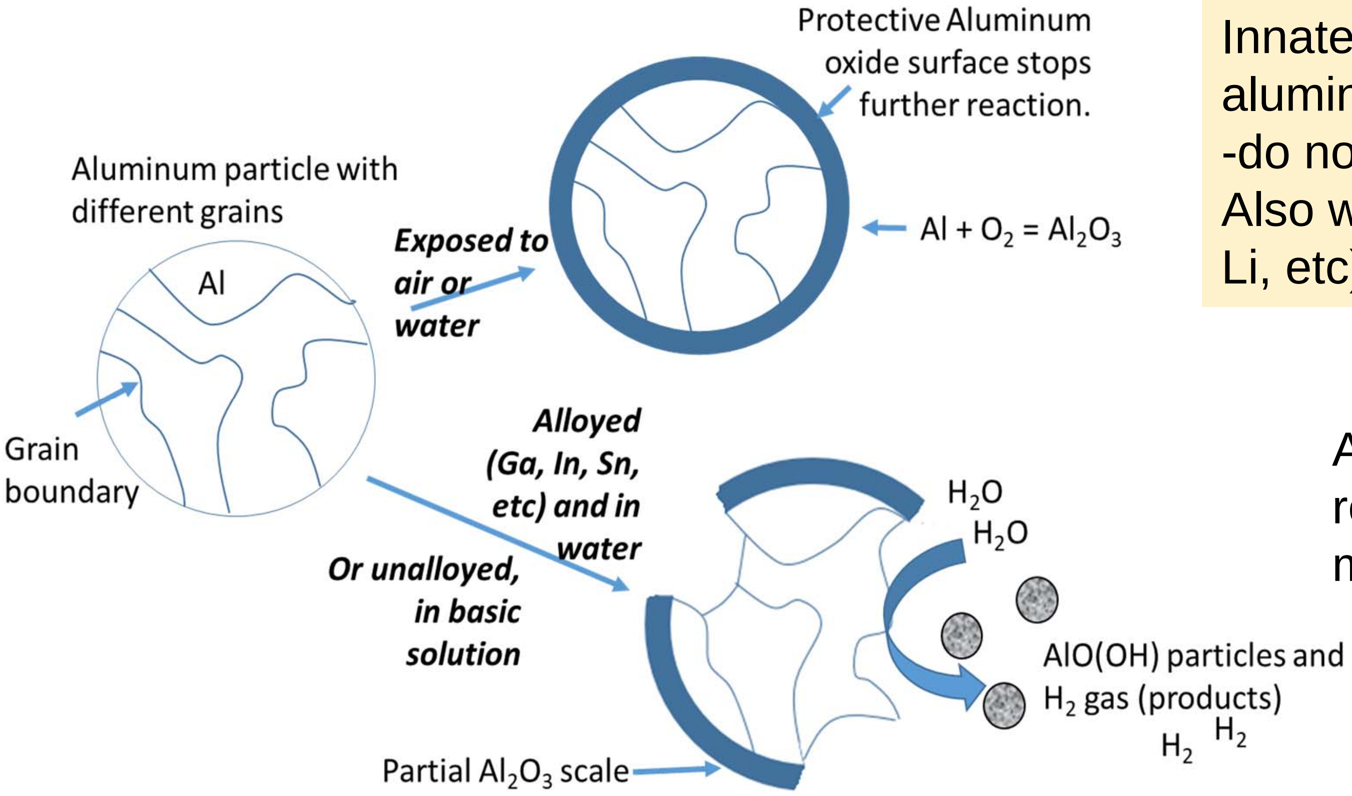
Electrolyzer splits H_2O into H_2 and O_2

H_2O + electricity = H_2 + ½ O_2 + heat (Q)

- Water splits at about 1.8 - 2 Volts
- Need source of electricity for voltage/current – about 60% efficient
- Systems typically dry and compress the H_2

Electrolysis technology used on naval ships for O_2 production

Hydrogen generation from aluminum and water



Innate electrochemical potential of aluminum sufficient to split water ---do not need additional electricity Also works with other metals (Mg, Li, etc)

Alloy aluminum so that it reacts with water to make H_2

$2Al_{(s)} + 6H_2O_{(l)} = 2Al(OH)_{3\,(aq)} + 3H_{2\,(g)} + Q$	(bayerite)	3.7 wt% H_2	(1)
$2Al + 4H_2O_{(l)} = 2AlO(OH)_{(aq)} + 3H_{2\,(g)} + Q$	(boehmite)	4.8 wt% H_2	(2)
$2Al + 3H_2O_{(l)} = Al_2O_{3\,(aq)} + 3H_{2\,(g)} + Q$	(alumina)	5.6 wt% H_2	(3)

Applications cases and evaluation criteria

Four application cases:

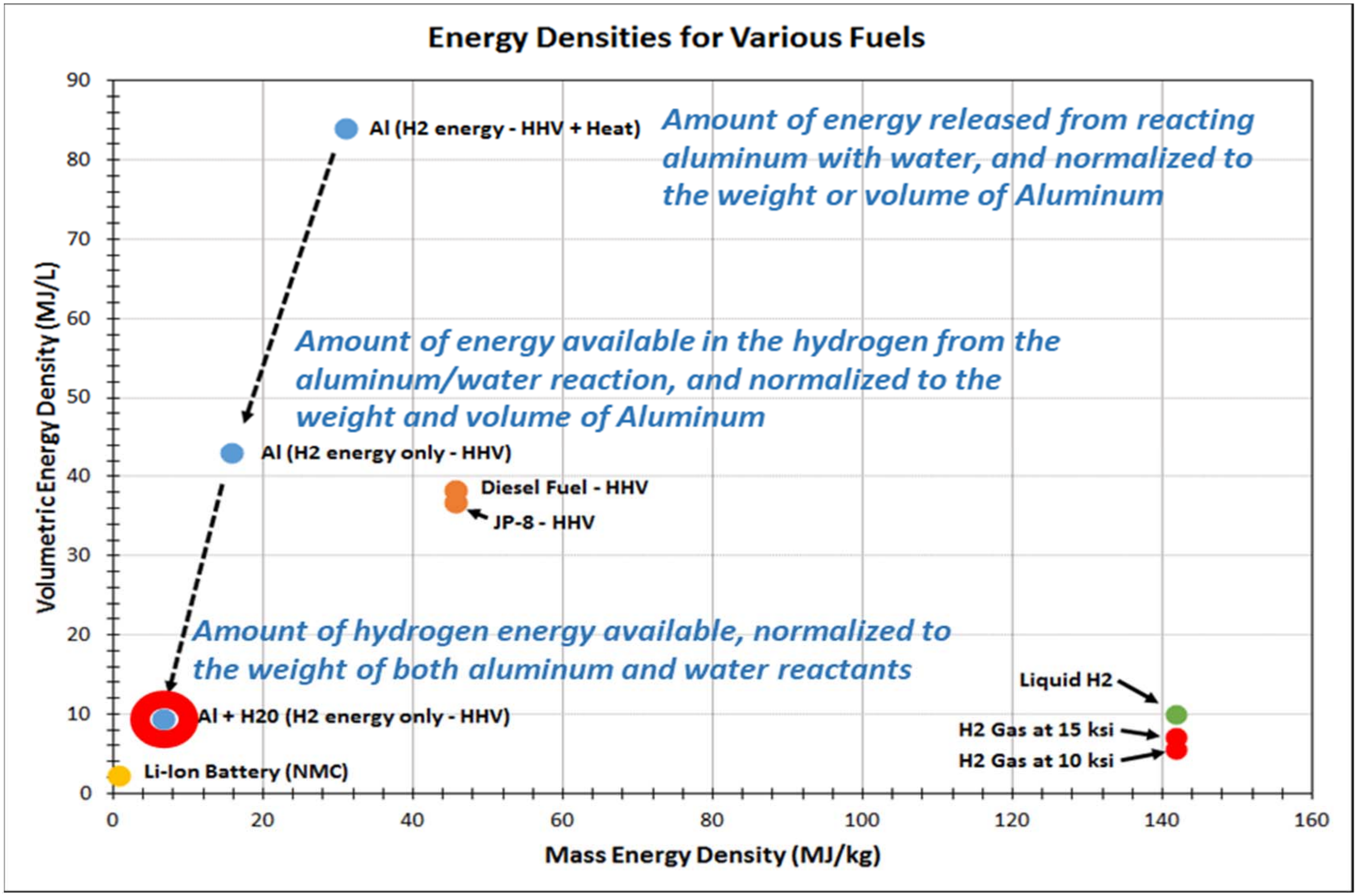
1. Small Scale Standalone Hydrogen Generation/ Dispensing System for small balloons or unmanned air vehicles
2. Small Portable Power Recharging for battery systems
3. Large Scale Standalone Generation/ Dispensing System for Light duty Vehicles, Other Fuel Cell based System Fueling
4. Medium Mobile Power Generation for Mobile generators

Evaluation criteria:

- the maturity/readiness of the technology
- potential capability of alternate/competing technologies
- logistics burden for use of the technology (weight, volume, estimated cost)
- thermodynamic/practical system limits of the technology
- Our own estimates of the weight of full energy generation systems.
- The cost of the technology

Aluminum water system is low energy

Aluminum often touted as having 83 MJ/Liter or 23 KWh/L



Amount of energy per liter or kg much lower when you consider volume and weight of water. Energy comes from H_2 product, not from Aluminum

Need a reactor

Anderson, WO 02/08118, 31 Jan 2002

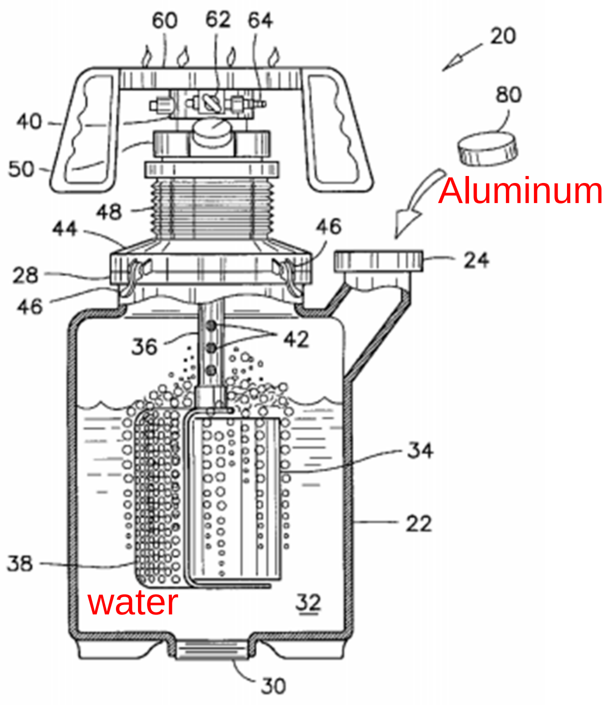


Table 1 – Summary of results for reaction experiments spanning target operating range.

Trial	T [°C]	P [MPa]	$\Delta G^{(i)}_{rxn}$ [kJ/mol]	Expected Byproduct	Actual Byproduct(s)
E1:	4	0.1	−887	$Al(OH)_3$	Elemental Al, $Al(OH)_3$
E2:	100	0.1	−897	AlOOH	AlOOH
E3:	4	6.9	−898	$Al(OH)_3$	$Al(OH)_3$
E4:	230	6.9	−880	AlOOH	AlOOH
Steam:	150	0.1	N/A	Al_2O_3	No reaction

- Water requirements/aluminum oxide products dependent on temperature and pressure, requiring reactor control

- Vessel has sufficient structure to hold pressure generated from the reaction
- And a requirement for heat (Q) rejection

See report for information on NRL's conceptual reactor weight and volume

UAVs and Balloons

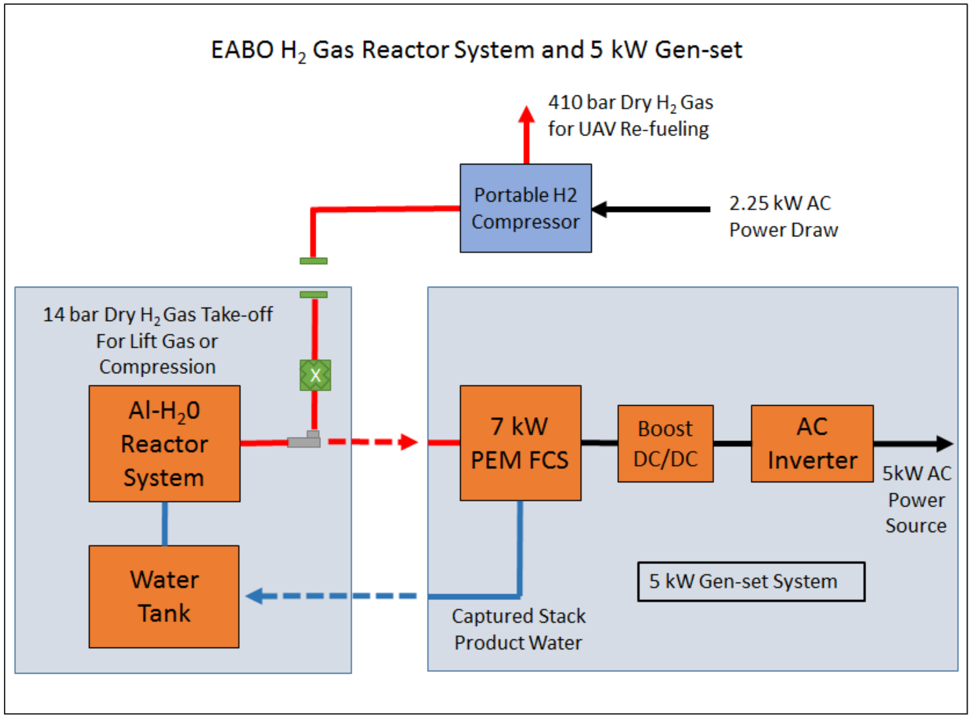
May be some benefits for UAV fueling and balloon filling if Al/H_2O reactor size and weight are low

Tier2 UAV refueling

Number of Tier2 UAV Fueling Events	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
21	3.7	0.90	40.8	23.6	44.1	44.2

Balloon

Number of Balloon Fueling Events	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
3	6.81	0.90	75.0	43.4	81.1	81.4

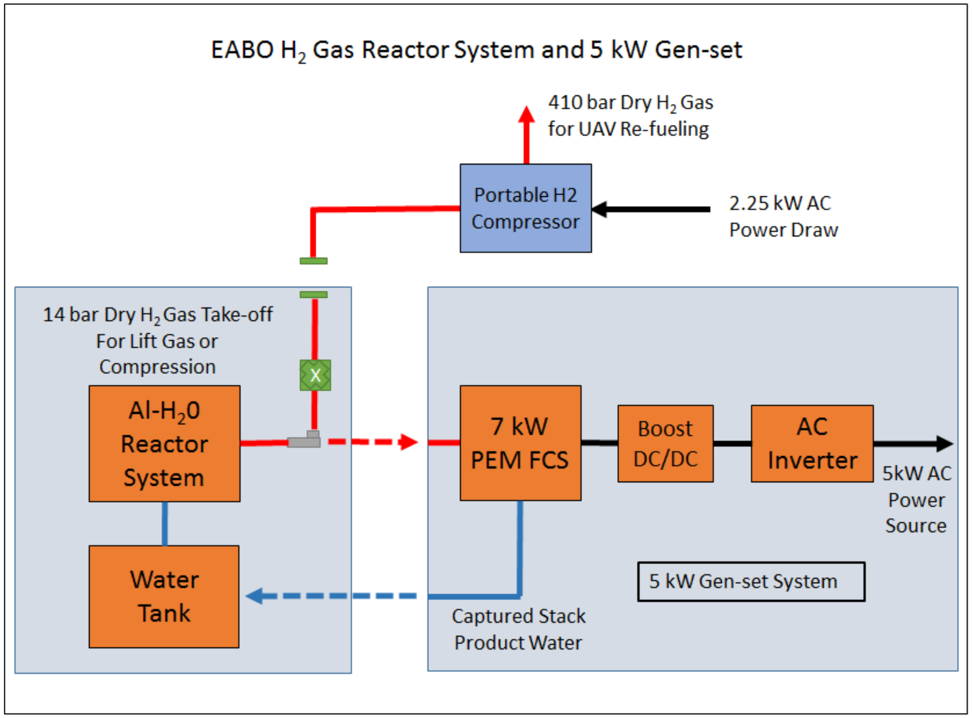


5 kW AC power for 7 days

5 kW AC power for 7 days

Advanced Medium Mobile Power Source (AMMPS) generator

158 kg of JP-8 fuel or 196 L.



Aluminum water system:
267 kg Al fuel + 105 kg water = 372 kg

Mission Operating Duration (hrs)	Avg. Use Profile AC Pwr (kW)	Mission H2 Usage (kg)	Avg. Expected Reactor Yield	Mass of Al Fuel Required (kg)	Al Fuel Packing Volume Required (L)	Stored Water Required (kg)	Stored Water Required (L)
168	2.2	24.2	0.90	266.6	154.3	104.7	105.0

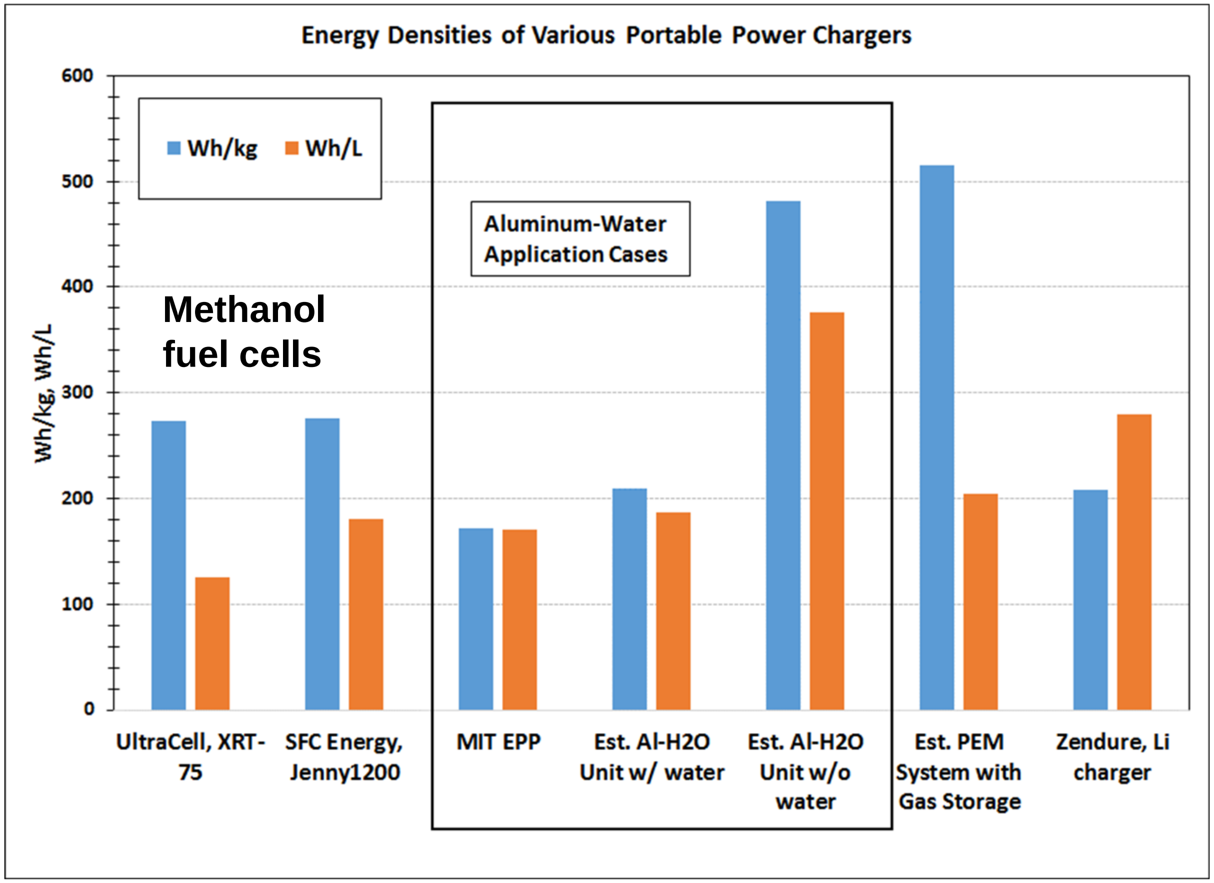
Logistics for 5 kW generator for 7 days

Power	Fuel	Duration	Logistics Footprint - Fuel
5 kW[1]	Al/H_2O Mix	7 Days (168 Hours)	  267 kg/154L 105 kg/105L **(22) 7L Ammo Cans and (7) 20L Water Cans**
	JP-8		 158 kg/196L **(10) 20L Fuel Cans**

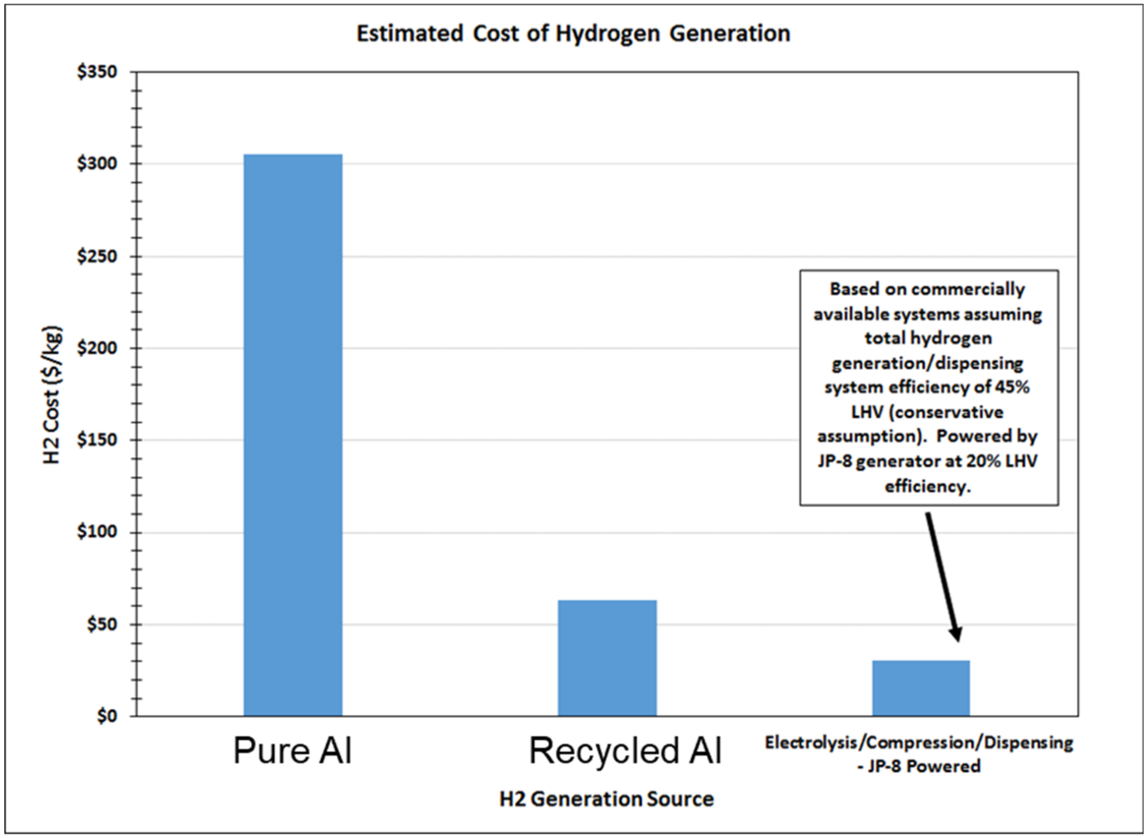
Power	Fuel	Duration	Logistics Footprint – Energy Conversion and Mobility
5 kW[1]	Al/H_2O Mix	7 Days (168 Hours)	  **(1) JLTV and (1) M101 Trailer mounted Al Reactor and Fuel Cell** Total load out = 754 kg/ 1,190L
	JP-8		  **(1) JLTV and (1) Trailer Mounted MEP-1030A Generator** Total load out = 513 kg/ 1,042L

Portable power charging stations

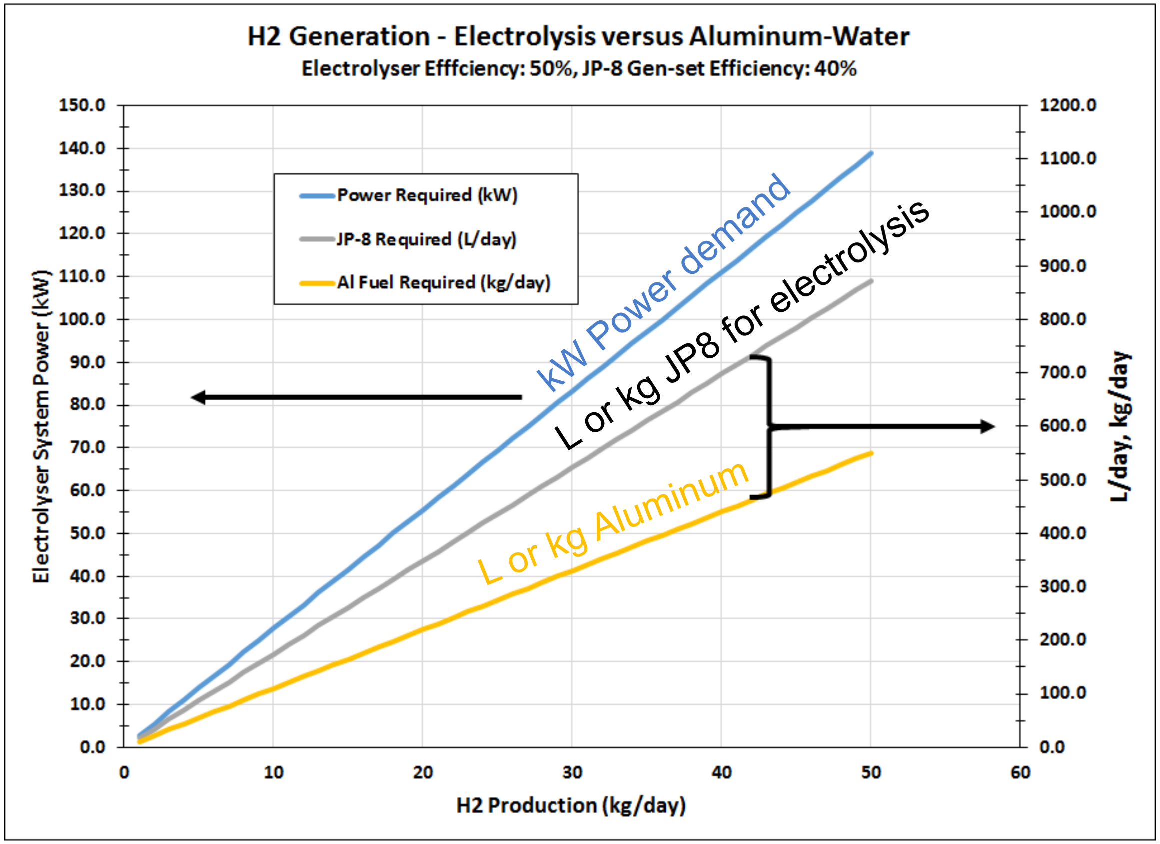
Maybe some volume and weight benefits over existing methanol fuel cells



Estimated costs of Al



H_2 generation at larger scale



Compare the amount of JP8 and kg Al needed for H_2 production at larger scale.

Both have very high demands – technology not attractive at scale

U.S. NAVAL RESEARCH LABORATORY

Similar to US Army GVSC analysis

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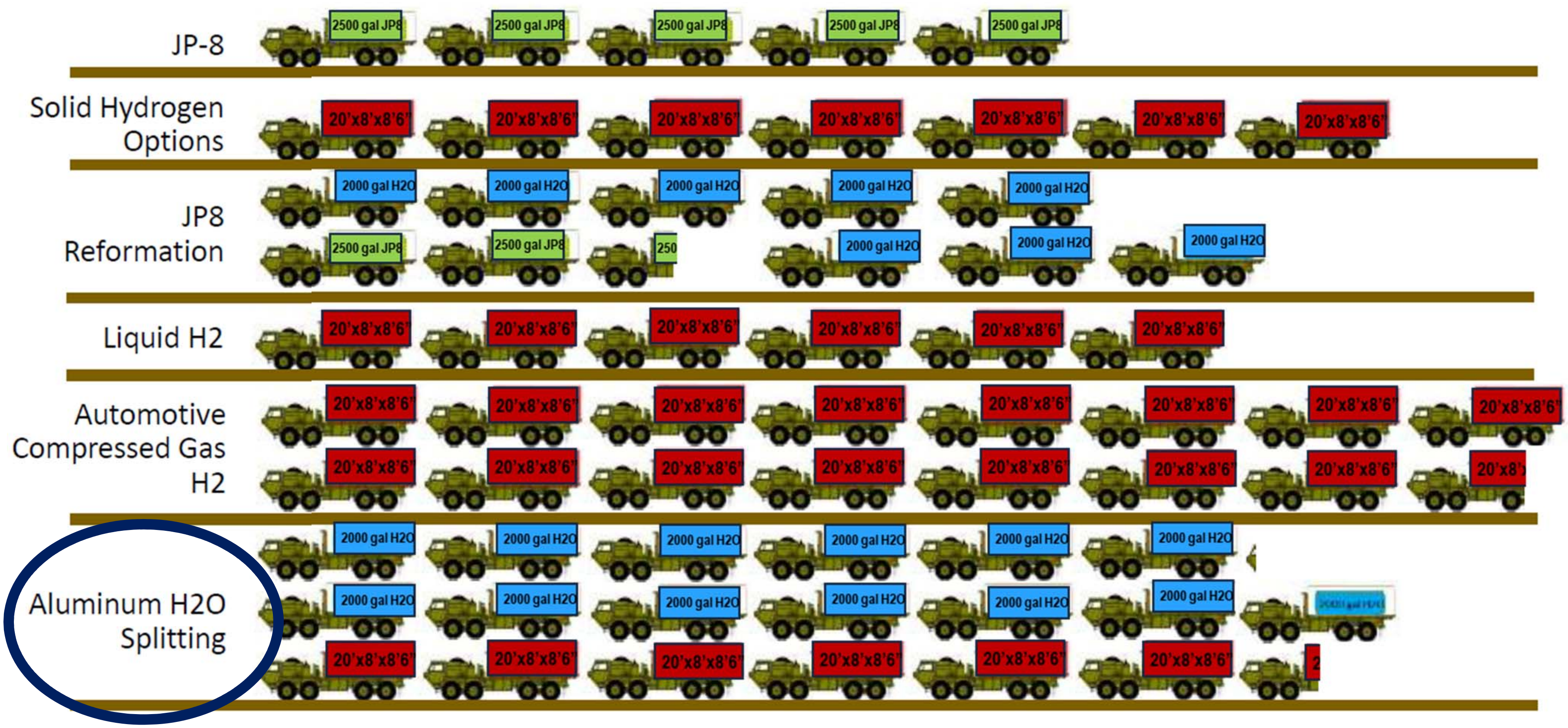
U.S. ARMY

HYDROGEN LOGISTICS OPTIONS ON A LARGE SCALE

DEVCOM GROUND VEHICLE SYSTEMS CENTER



Medium to large mobile power is not compelling for Al/H_2O even if water can be scavenged.

Kevin.s.centeck.civ@mail.mil

M1120 LHS Capacities, no trailers. Corrected for improved fuel consumer efficiency and H2 to JP-8 energy difference. Compression of H2 and fuel consumed by M1120 ignored.

Consistent with 2008 DOE analysis

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

J. Petrovic and G. Thomas
Los Alamos and Sandia National Labs

Version 1.0 - 2008
Page 1 of 26

Purpose: "evaluate the potential of aluminum-water reactions for the production of hydrogen for on-board hydrogen-powered automotive applications"

"The concept of using the aluminum-water reaction to provide onboard hydrogen for hydrogen-powered vehicles presents a number of difficulties."

- Low hydrogen content
- Production rate
- Cost

"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"

Recommendations for Al/H_2

Case Study	H2 Quantity	Applications	Potential Application Feasibility	Potential Capability of Alternative Technologies
Small Scale Standalone Hydrogen Generation/ Dispensing System	2-4 kg/day	Small Balloons or UAVs	Capable of quickly producing hydrogen in the battlefield, can combine multiple units for higher H2 kg/day	• Bulk cylinder-stored (K,T bottles) hydrogen is a much heavier option with negative logistics impacts and safety concerns • Water electrolysis is possible, but requires electrolyzer systems, and sufficient power generation, and JP8 fuel at point of use
Small Portable Power Recharging	<0.1 kg/re-charge	Battery Recharging	Would offset extra carried batteries with a small, quiet, and light weight battery charger	• If small scale hydrogen generation/ compression is available in an EABO, then gas refillable canisters could be a better alternative for hydrogen supply • Needs to be benchmarked against other fuel cell recharging systems available in the market place
Large Scale Standalone Generation/ Dispensing System	5-50 kg/day	Light duty Tactical Vehicles, Other Fuel Cell based System Fueling	Technically feasible alternative to diesel-fueled electrolysis systems, further comparative analysis required of equipment footprint, and logistic options	• Water electrolysis is a more mature alternative, and likely more cost effective, but requires sufficient power generation infrastructure and JP-8 fuel availability
Medium Mobile Power Generation	~2 kg/refuel	Mobile generators	Inferior for power-only applications, considerable research still required to assess secondary uses for reaction heat	• Diesel generators are superior, improving with hybridization, and could also offer combined heat-and-power alternatives

Table I: Feasibility of aluminum-generated hydrogen for four different USMC missions.

NRL conceptual systems

Looks good! present funding:
Lincoln labs
ONR Tech Solutions

Maybe!
General Atomics
ONR - J. Parker

Not looking so good
Army GVSC has looked at vehicle/tank power extensively and found the same – K. Centeck

Nope, don't bother
Just use the diesel generator

Conclusions & Final Thoughts

Al/H_2O is not a high energy system

- Can only consider H_2 produced by the Al for energy
- Logistics burden might be lightened if water can be scavenged in the field.
- Is it possible to scavenge for scrap aluminum as well?

Work needed on hydrogen fuel cells

Reactor designs can be improved to optimize reactions

Large amounts of H_2 unlikely to be used on the battlefield soon.

Shipping aluminum powder might have higher safety benefit that shipping gaseous or liquid H_2

- Key for some applications which might have very low risk tolerance
- Safety must be considered around aluminum/H_2O reactor

Several programs presently funded for Al/H_2O technology

Results will be the best indicator of the feasibility of Al/H_2O technology

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Acknowledgements

This work was funded by J. Parker. ONR Code 33

We are grateful to MIT Lincoln Labs and General Atomics for technical input