# Chemical Hydride Hydrogen Sources for Small Fuel Cells

## Final Report

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September 30, 1997

US. Army Research Office

Contract No. DAAG55-97-C-0023

Magnic International, Inc.

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# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB NO. 0704-0188*

| 1. AGENCY USE ONLY *(Leave blank)* | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVFRED |
|---|---|---|
| | September 30, 1997 | Final Report Feb 1 - Aug 30, 1997 |

4. TITLE AND SUBTITLE

Chemical Hydride Hydrogen Sources for Small Fuel Cells - Final Report

5. FUNDING NUMBERS

DAAG55-97-C-23

6. AUTHOR(S)

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

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6895FR

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

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

<u>Report developed under SBIR contract.</u> This report details and investigation into the feasibility of thermal decomposition (non-hydrolytic) of aluminum hydride ($AlH_3$) for hydrogen production. A unique new process, referred to as the self-sustaining (SS) reaction, was developed, along with a prototype generator and cartridges of $AlH_3$ for use in the generator. Tests performed indicate repeatable, rapid hydrogen production and a safe reaction. Issues of controllability are addressed for future work.

14. SUBJECT TERMS

Hydrogen, fuel cells, hydride, aluminum hydride, self-sustained reaction, portable power

15. NUMBER IF PAGES

25

16. PRICE CODE

| 17. SECURITY CLASSIFICATION OR REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| UNCLASSIFIED | UNCLASSIFIED | UNCLASSIFIED | UL |

NSN 7540-01-280-5500

**Standard Form 298 (Rev. 2-89)**
Prescribed by ANSI Std. 239-18

## 1. Project Objectives

Magnic International Inc. (MII), a small business based in Durham, NC, has collaborated with Research Triangle Institute (RTI) and scientists from the State Scientific Center of the Russian Federation, in Moscow, to investigate the production of hydrogen from metal hydrides. This effort was undertaken in response to a U.S. Army requirement for a hydride-based, compact hydrogen source to produce high-grade hydrogen to power small fuel cells. The power range of the fuel cells addressed was between 20 W and 1 kW. Several hundred watt-hours of energy production, at 50% energy conversion efficiency (fuel cell efficiency), was the designated energy production target.

The proposal for this effort initially recommended an investigation into the hydrolytic dehydriding of light metal hydrides such as LiH, $LiBH_4$, $LiAlH_4$, $NaBH_4$, and $NaAlH_4$. Such a reactor was designed and built in an effort which ran partly in parallel with this project. That successful effort yielded significant insight into the hydrolysis of metal hydrides for hydrogen production, in particular $NaAlH_4$, as characterized by the reaction,

$$NaAlH_4 + 4H_2O \Rightarrow NaOH + Al(OH)_3 + 4H_2 + 111.2\frac{kJ}{mol\ H_2} \qquad \textbf{(1)}$$

A complete description of the hydrolysis of $NaAlH_4$ can be found in the Final Report issued for the Small Business Technology Transfer topic <u>Improved Power Sources: Phase I</u> (Serebrennikov, et.al., 1997).

Because of the understanding gained in that effort, the focus of this project was reoriented to a "dry" dehydride reaction. In particular, the project team investigated the thermal, pyrolytic, decomposition of aluminum hydride ($AlH_3$). In general, the thermal decomposition of aluminum hydride ($AlH_3$) is characterized by the endothermic reaction

$$AlH_3 \Rightarrow Al + \frac{3}{2}H_2 \quad (\Delta H = -2.7\frac{kcal}{gmole}) \qquad \textbf{(2)}$$

which takes place in the presence of heat.

One obvious advantage of dry pyrolysis is the increased yield of hydrogen per unit mass of reagents used. For example, stoichiometric hydrolysis of $NaAlH_4$ will require approximately 16 g of reagents ($NaAlH_4$ and $H_2O$) per gram of hydrogen produced. In practice, the excess of water (~100%) usually required for complete hydrolysis reduces hydrogen yield to almost 1 g per 25 g of reagents used. Thermal pyrolysis, on the other hand, produces a stoichiometric amount of hydrogen with a yield of 1 g hydrogen per 13.5 g of $NaAlH_4$ reagent. Yield of hydrogen is even higher with $AlH_3$: 1 g/10 g reagent. For a soldier pack application, thermal pyrolysis of hydrides is likely to provide a more compact system compared to the hydrolysis approach.

Another advantage of the thermal pyrolysis is that the process does not produce steam vapor in the $H_2$ gas , thereby eliminating any need for condensation of water as required in the hydrolysis process. Thermal pyrolysis is inherently attitude insensitive and is applicable in a wide temperature range including freezing conditions.

## 2. Work Performed

During the course of this project, different hydrides were examined to determine the best hydride for hydrogen production from thermal decomposition. A new approach to the thermal decomposition of $AlH_3$, the self-sustaining reaction, was developed. With this new approach, original methods of material packaging and synthesis were investigated, and a new generator design was completed. Numerous tests were conducted to investigate the behavior of $AlH_3$ in this new reaction for thermal decomposition.

### 2.1 Selection of Hydride for Thermal Decomposition

Among various hydrides considered in the course of this effort, $AlH_3$ has the second highest mass yield of hydrogen, and requires the least heat for thermal decomposition. Characteristics of $AlH_3$ in comparison with other hydrides are shown in Table 1.

**Table 1. Properties of Simple and Complex Hydrides of Al and Mg**

| Hydride | $-\Delta H$, kcal/mol | $\rho$, g/cm$^3$ | $H_2$, % mass | $\rho_{H2}$, g/cm$^3$ | Temp. of Dehydriding, °C | Vol. $H_2$, ℓ/kg |
|---|---|---|---|---|---|---|
| $AlH_3$ | 2.7 | 1.48 | 10.0 | 0.148 | 120-180 | 1120 |
| $LiAlH_4$ | 24.7 | 0.917 | 10.53 | 0.097 | 150-200 | 1176 |
| $NaAlH_4$ | 27.0 | 1.128 | 7.4 | 0.095 | 180-230 | 829 |
| $MgH_2$ | 19.1 | 1.145 | 7.6 | 0.11 | 250-400 | 851 |

In addition to low energy requirement for thermal decomposition, $AlH_3$ is stable in air. Thermal decomposition of $AlH_3$ has been studied extensively in the literature (e.g. Herley et al., 1981). In addition, the Russian scientists included in the research team had considerable prior laboratory experience in the dehydriding of $AlH_3$. Aluminum hydride was therefore chosen for further investigation.

### 2.2 The Self-Sustaining Reaction

One particular property associated with $AlH_3$ that is favorable for the dry dehydriding process is the ability of the metallic aluminum produced to react exothermically with metals from the iron group (Group VIII in the Periodic Table, e.g. Fe. Ni, Co.) That reaction can be shown as

$$nAl + M \Rightarrow Al_nM + heat. \tag{3}$$

The heat produced by this reaction can be used to drive the endothermic $AlH_3$ dehydriding reaction. The quantity of heat liberated in reaction (3) depends upon the specific alloy $Al_nM$ formed in the reaction. The heat produced for different Al-M products is shown in Table 2.

**Table 2. Self-Sustaining Reaction Products**

| Inter-metallic compound | AlFe | $Al_2Fe$ | $Al_3Fe$ | AlCo | $Al_2Co$ | AlNi | $Al_3Ni$ |
|---|---|---|---|---|---|---|---|
| Quantity of heat produced (kcal/mol) | 9.3 | 17.3 | 24.3 | 23.2 | 36.2 | 25.1 | 33.4 |

The production of heat from the aluminum-metal alloying reaction can be manipulated to drive the endothermic dry $AlH_3$ dehydriding process to completion with very little excess heat. The overall reaction of thermal dehydriding of $AlH_3$ in presence of a metallic species M may be represented as a self-sustaining (SS) reaction:

$$nAlH_3 + M \Rightarrow Al_nM + \frac{3n}{2}H_2 + heat \qquad \textbf{(4)}$$

Although the thermal decomposition reaction can proceed at relatively low temperatures, the heat-producing, alloying reaction occurs at temperatures of 450 to 600°C. Once initiated, the SS reaction ideally would propagate through the solid mass as a thin hot zone at this temperature. The dehydrided mass behind the hot zone will, however, be at much lower temperature due to the endothermic reaction cooling, estimated to be about 300 °C.

The overall process is shown schematically in Figure 1 for two geometric modes of SS reaction initiation in cylindrical cartridges: (a) initiation in a central core of the cylinder, and (b) initiation at one end of the cylinder. The heat losses will be minimized by allowing the reaction front to propagate radially outward as in mode (a). Both the kinetics of the SS reaction as well as the heat transfer characteristics leading to heat losses from the hot SS reaction front are important in self sustained propagation of the SS and $AlH_3$ dehydriding reactions.

The feasibility of the aluminum-metal SS reaction was confirmed by the Russian scientists at the State Scientific Center of the Russian Federation in Moscow. The speed of SS reaction front was found to be relatively fast (1 mm/sec or less) with complete decomposition of a 24 g $AlH_3$ cartridge within 40 seconds. This fact indicates that the induction period observed in low temperature isothermal decomposition studies (Herley, et.al., 1981) is practically eliminated when a high temperature SS reaction is used as the heat source for the thermal dehydriding reaction (see **Section 3. Results Obtained**).

By adjusting the proportion of the metallic species M and $AlH_3$ in the solid mixture, the heat produced in reaction (4) is used to maintain the temperature of the entire solid mass at or greater

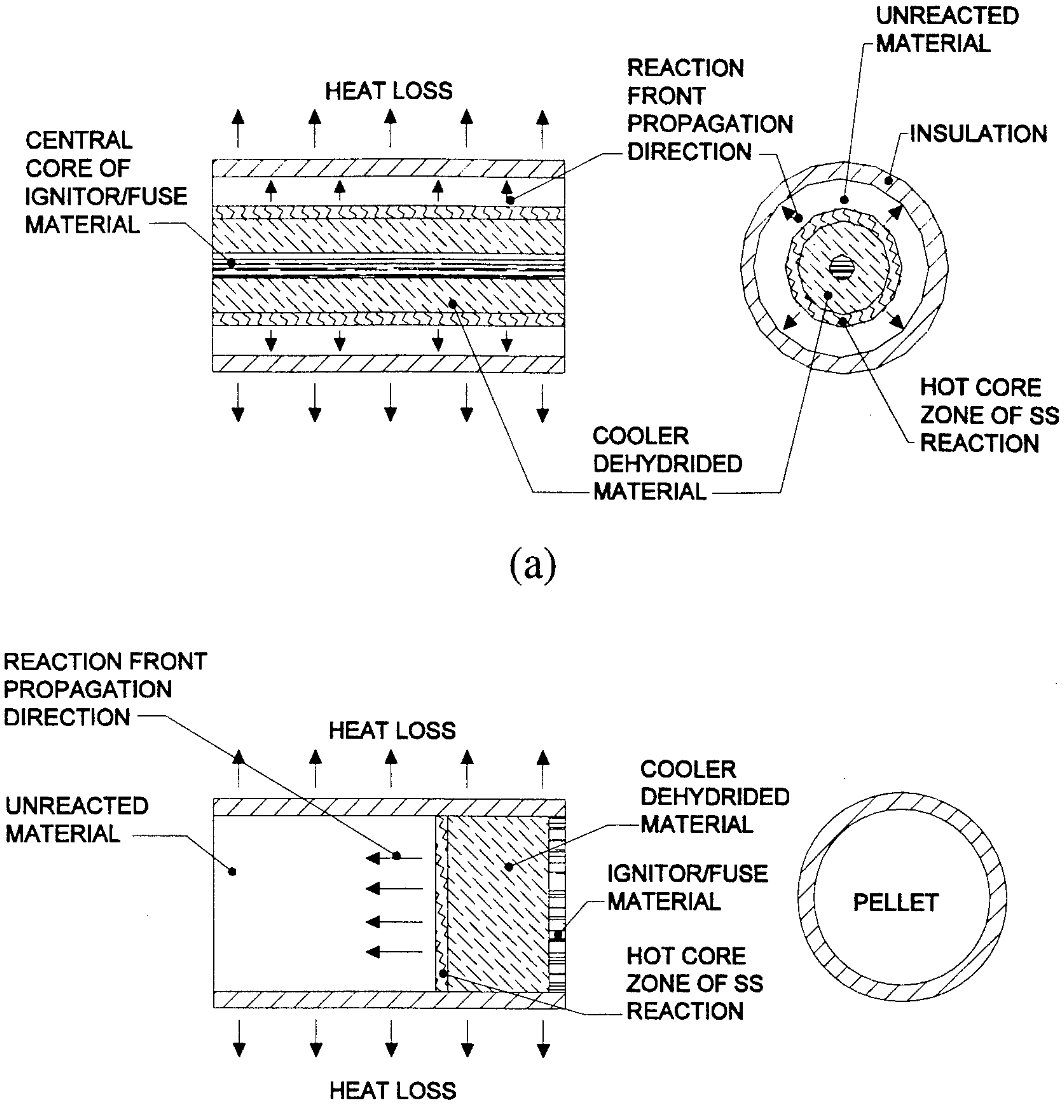


**Figure 1:** Partial Dehydridization of Cylindrical Cartridges (a) Ignition Propagating from Core (b) Ignition Propagating from End

than the desired $AlH_3$ thermal decomposition temperature. Since the overall $AlH_3$ dehydriding reaction is self-sustained, it continues to completion once initiated.

Nickel was chosen from the Group VIII elements for the alloying reaction in this study. As shown in Table 2, Fe produced lower heat per mole than the equivalent Ni alloy. Since cobalt is toxic, nickel is the best choice. The ideal ratio $AlH_3$:Ni lies in the range 2:1 to 2.2:1. If the ratio is greater than 2.2:1 the SS reaction does not go to completion because there is not enough heat for the SS process. The effect of various ratios of hydride to Ni are shown in Table 3.

**Table 3: Effect of varying $AlH_3$:Ni Ratio on SS Heat Production**

| Ratio $AlH_3$:Ni | Inter-metallic product | ΔH, kcal | Q, kcal/gram $AlH_3$-Ni Compound |
|---|---|---|---|
| 1:1 | AlNi | 25.3 | 0.284 |
| 2:1 | $Al_2Ni$ | 26.6 | 0.224 |
| 3:1 | $Al_3Ni$ | 27.86 | 0.187 |

## 2.3 Prototype Generator Design

Dry dehydriding of $AlH_3$ liberates hydrogen quickly. Tests have shown that a volume of several liters can be produced in less than a minute. To provide safe conditions for the experimental reactions, a generator was constructed which could contain hydrogen resulting from dehydriding of up to 75 grams of the SS compound. Such a generator was constructed of stainless steel (ASTM 305 austenitic stainless steel, Russian equivalent X18H10T) by Russian team members. The design of this reactor is shown in Figure 2.

The generator body and flanged lid are built from 305 stainless steel with a wall thickness of 1 mm (0.0394".) The diameter of the body is 60 mm (2.362".) The flanged lid is sealed to the body with eight bolts. Gas is prevented from leaking at the lid with a flat gasket. A valve and a pressure gauge mounted to the top of the unit allow the hydrogen to be drawn off and the interior pressure to be monitored. This unit was later modified at RTI to accept thermocouples inserted into the interior of the body. In tests, the generator has been pressurized with argon gas to 30 atmospheres, which is two and a half times the prototype nominal working pressure of 11 atmospheres. The generator was found to provide a hermetic seal at 30 atmospheres. It was also found to hold a vacuum at 28" of Hg.

To contain the reaction in a manner which minimized generator cleaning requirements and facilitated generator reloading, a cartridge design was developed which would fit into the generator and contain the SS compound and the reaction by-product, which is an Inter-metallic of Al and Ni produced in accordance with reaction (3). Since the SS reaction requires an initial amount of energy in the form of heat, a method was devised to remotely start the reaction.

### *2.3.1 Cartridge Design and Preparation*

For tests conducted both in Russia and at RTI, 24 g of the $AlH_3$-Ni powder was used to construct cartridges which could produce over 13 ℓ of $H_2$. The hydride $AlH_3$ used for testing was produced from the reaction of Finholt (Finholt, et.al., 1947) with solvent removal. $AlH_3$ and Ni powder were mixed in a centrifugal tumbler in a ratio of 1:1 by mass. The mixing process took place over a period of 10 hours. The Ni powder consists of particles of between 5 and 8 microns in size.

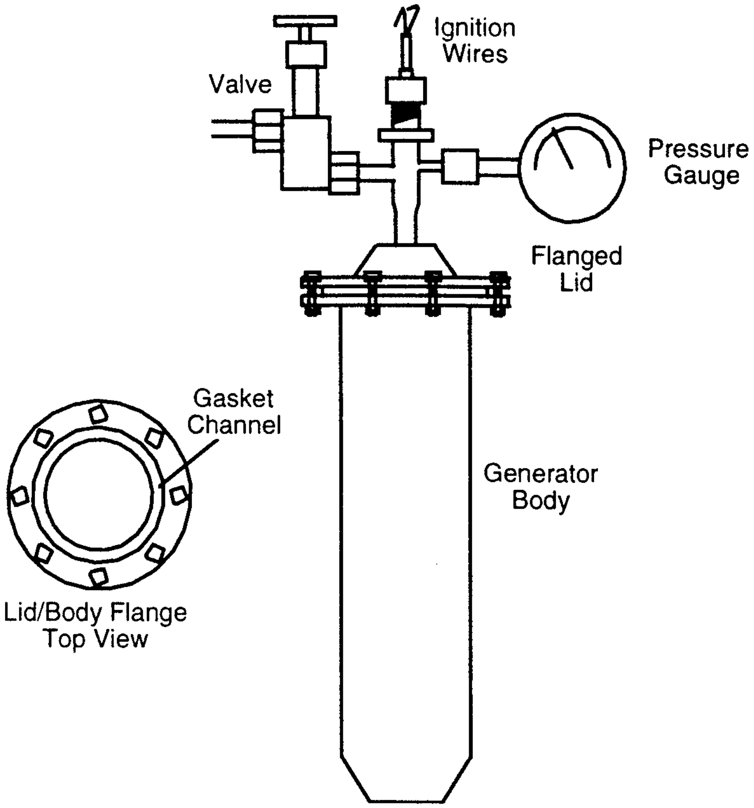


**Figure 2**. Prototype Generator Design

Initiation of the SS reaction was accomplished by igniting a mixture of titanium and boron powder (Ti,B) to provide heat. The geometry of the reaction is as shown in Figure 1, mode (a). The Ti,B powder forms a core surrounded by the $AlH_3$-Ni compound, as illustrated in Figure 1a. To create a "charge", 24 g of the $AlH_3$-Ni compound were pressed into a die at pressures of 50-250 Mpa. The die forms a 40 mm long cylinder with a hollow core. The core diameter is 8 mm (0.31".) Into this hollow core are inserted two 7mm (0.276") diameter rods of Ti,B compound.

The Ti,B rods are prepared by mixing Ti,B powder with 20% by mass of 5% polyvinyl alcohol. This compound is pressed into the desired shape, and then dried for 10-24 hours to add mechanical strength. One of the rods is between 8 and 12 mm in length, and is formed with an embedded nichrome wire of 2-4 mm in length with a diameter of 0.1 mm. The nichrome wire is joined with copper wire within two ceramic shells which are stabilized to provide strain relief for the rod. The second rod of the strengthened, pressed Ti,B mixture is 28-32 mm in length.

After the Ti,B rods are inserted into the hollow core of the SS compound cylinder, the charge is placed into a stainless steel cylindrical shell 50 mm H x 25 mm ID (1.97" H x 0.98" ID.) Perforated end caps hold the assembly within the shell, and provide egress for hydrogen gas and the copper ignition wires. The result is a cartridge of SS compound which can be ignited from a remote source for immediate hydrogen production.

The cartridges are held in a magazine which consists of two steel disks. The disks accommodate the cartridges in cavities designed for the purpose. Three bolts clamp the disks together. This arrangement comprises a magazine which is inserted into the generator. The magazine and cartridge are shown in Figure 5. The copper wire exiting the individual cartridges connects with copper wire in the cap of the generator, through which external electrical power is passed to achieve ignition of the Ti,B material.

The reaction is initiated through the application of 15-20 dc volts for a period of 1 second. The magnitude of the voltage required is a function of the resistance of the nichrome wire. In earlier experiments, the Ti,B ignition compound could be started with 4 volts from the heat generated by a standard tungsten bulb element, such as are commonly used in flashlights. The available nichrome wire required a higher voltage to initiate the Ti, B compound thermal reaction. The Ti,B thermal reaction generates localized temperatures of between 1000 and 1200°C.

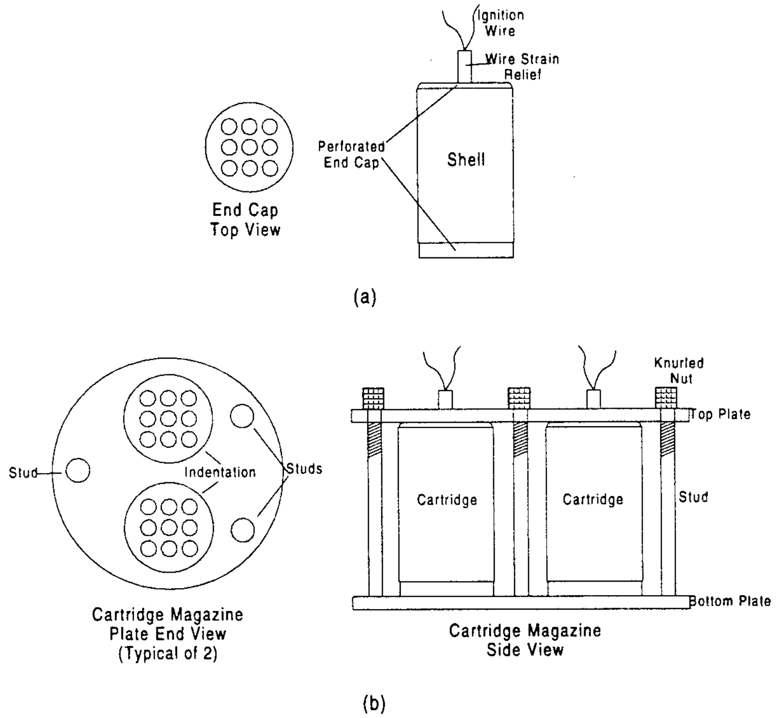


**Figure 3**. Cartridge and Magazine Detail (a) Cartridge (b) Magazine

## 2.4 Hydrogen Generation Tests

Numerous tests were conducted in the course of this work. Experimental verification was obtained for optimum ratios of $AlH_3$ and Ni, hydrogen production from assembled cartridges, predicted temperature and pressure profiles in the generator, and safety issues associated with hydrogen production from the SS reaction. From these tests, which are described in **Section 3. Results Obtained**, important information was gained about reaction behavior, and design parameters for future work were indicated.

## 3. Results Obtained

A number of 24 g $AlH_3$:Ni cartridges and the prototype generator, both as described in section 2.3, were used to characterize hydrogen generation under a variety of firing conditions. Early tests were performed at the State Scientific Center of the Russian Federation (SSC-RF) to determine the kinetics of the dry dehydriding reaction, the total amount of hydrogen released, consequent generator pressure increase, and the temperatures generated by the reaction. Temperatures were measured at the hydride cartridge surface as well as at the outside surface of the stainless steel generator. These tests also evaluated the effect of pressure in the generator prior to firing. The results were confirmed by several tests conducted at the Research Triangle Institute. Additional experiments were conducted at RTI to investigate the effect SS reaction initiation in the presence of air. The concentration of the impurities present in the hydrogen generated was measured to determine the overall purity of the hydrogen produced.

### 3.1 Test Results from the State Scientific Center of the Russian Federation

Prior to cartridge manufacture, experiments at the SSC-RF were conducted to determine an optimum $AlH_3$:Ni ratio for sustaining the dehydriding reaction while producing the most hydrogen per unit weight of the reagent material. A greater proportion of $AlH_3$ will naturally produce a greater amount of hydrogen as long as the reaction can be sustained. As described in Section 2.2, the optimum SS reaction was found to occur when the ratio of $AlH_3$:Ni was in the range 2:1 to 2.2:1. At a ratio greater than 2.2:1, not enough heat was generated to sustain the SS reaction, whereas at lower ratios hydrogen production was lower.

Tests were also conducted to determine the best reaction to be used for SS ignition. The reaction of Ti and B was selected because of its low activation energy. In early tests, the Ti,B compound was ignited using filaments from a flashlight bulb and a DC voltage of approximately 4 volts. The addition of nichrome wire was in response to the need for a manufactured cartridge.

Several tests were conducted with 24 g $AlH_3$:Ni cartridges with a 4.5 g Ti,B ignitor core. These cartridges are expected to produce about 13 liters of hydrogen at standard conditions. After the cartridge magazine was loaded into the generator, the generator was evacuated to 29.9" Hg. Cartridges were tested in the generator under conditions of varying pressure. Specifically, the reaction was started under vacuum (29.9" Hg), at atmospheric pressure in inert gas (argon) and at 5 atmospheres in inert gas (argon). Argon was introduced into the generator after a vacuum was drawn. Varying pressure conditions and reaction duration for each test are shown in Table 4.

Test 1 was performed with a single cartridge in the generator. All other tests were made with two cartridges. Tests 1-3 were made under vacuum, tests 4-7 in argon at atmospheric pressure, and tests 8-9 in argon at 5 atmospheres. In tests 10-13, after the first cartridge was spent, the pressure in generator was reduced to 2 atmospheres (simulating fuel cell hydrogen demand), and then the second cartridge was started. In tests 14 and 15, a second cartridge was fired without reducing gas pressure.

**Table 4: Cartridge Test Data from Prototype Dry Hydride Hydrogen Generator**

| Test No. | Cartridge ID | Date | Reaction Time (Sec.) | Comments |
|---|---|---|---|---|
| 1 | 27 | 6/16/97 | 31 | One cartridge, vacuum |
| 2 | 28 | 6/17/97 | 60 | Two cartridges, vacuum |
| 3 | 29 | 6/17/97 | 30 | Two cartridges, vacuum |
| 4 | 30 | 6/18/97 | 35 | Two cartridges. Atmospheric pressure |
| 5 | 34 | 6/18/97 | 38 | Two cartridges. Atmospheric pressure |
| 6 | 37 | 7/2/97 | 32 | Two cartridges. Atmospheric pressure |
| 7 | 38 | 7/2/97 | 39 | Two cartridges. Atmospheric pressure |
| 8 | 39 | 7/2/97 | 60 | Two cartridges, Ar at 5 atm |
| 9 | 42 | 7//297 | 31 | Two cartridges, Ar at 5 atm |
| 10 | 43 | 7/3/97 | 33 | Two cartridges |
| 11 | 47 | 7/3/97 | 50 | Two cartridges |
| 12 | 48 | 7/3/97 | 40 | Two cartridges |
| 13 | 52 | 7/3/97 | 40 | Two cartridges |
| 14 | 53 | 7/3/97 | 31 | Two cartridges |
| 15 | 59 | 7/3/97 | 36 | Two cartridges |

The following conclusions may be drawn from thermal and pressure data gathered during the tests:

1) The pressure in the generator has no influence on the SS reaction. The reaction takes place with equal facility in a vacuum, or under pressure of up to 20 atmospheres.

2) A single cartridge produces approximately 13.5 $\ell$ of $H_2$, which will create a pressure of 11 atmospheres in the generator.

3) The heat produced from the ignition of 4.5 g of the Ti-B ignition compound is 3.12 kcal. Total heat production from the cartridge, including the ignition reaction and the SS dehydriding process, is approximately 6.2 kcal.

4) Firing a single cartridge will produce temperatures of 100-110°C in the region of the generator surface nearest the cartridge. Dispersion of the heat through the generator wall

eventually produced a generator surface temperature of 68°C. From this observation, we can conclude that the ignition of a single cartridge in close proximity to an unfired cartridge does not cause a reaction to begin in an unfired cartridge.

5) The productivity of the generator can greatly exceed the nominal target of 300 W, which assumes a production rate of 170 liters per hour (lph.) Hydrogen can be produced at the rate of 800 lph if the cartridges are ignited at 1 minute intervals. To produce 300 W of power, cartridges can be fired at 5 minute intervals.

### 3.2 Research Triangle Institute Test Results

Tests were performed at RTI in late July and in August. Tests performed in late July demonstrated the function of the generator to U.S. Army Research Office (ARO) project officers, and also confirmed the results obtained in Russia at the SSC-RF. The August tests were undertaken to determine the effect of initiating the SS reaction in the presence of air, rather than in the presence of inert gas or in a vacuum.

Tests were conducted in the period July 28- August 2 at RTI. A trial test was conducted without computer recording to test the ignitor power supply as well as additional fittings used to set up generator evacuation and nitrogen backfilling operations. The test was conducted with two cartridges loaded in the generator with 1 atm initial nitrogen pressure. Nitrogen was introduced after evacuating the generator to 28" Hg. Two nitrogen purge cycles were used to remove air from the generator between vacuum pump operations. Upon firing the first cartridge the generator pressure went up to 11 atm. The hydrogen was released to reduce the generator pressure to 5 atm. The second cartridge was then fired. The pressure increased to 14 atm, thus confirming hydrogen generation capacity of the cartridges.

A second test provided a demonstration to ARO project monitors Dr. Richard Paur and Dr. Peter Fedkiw. The same sequence as in the trial test was repeated for the demonstration. This test used automatic computerized data recording of the generator pressure as well as generator outside surface temperature near the cartridge location. Again two hydride cartridges were loaded in the generator. The generator was evacuated and backfilled with nitrogen two times. The generator was then evacuated for the third time and was left in vacuum before firing the first cartridge.

Figure 4 shows the pressure response over time. Pressure rose from -12 psig to 147 psig. Pressure reached 90% of the maximum value in 35 seconds, and peak pressure occurred at 83 seconds. Figure 5 shows the generator surface temperature rise with time. The temperature rose from ambient to 82°C in 88 seconds.

After a cooling period surface temperature was reduced to 57°C. The pressure in the generator was reduced to 90 psig by venting hydrogen. The second cartridge was then fired in hydrogen atmosphere within the generator. The pressure rose from 90 to 217 psig with a peak

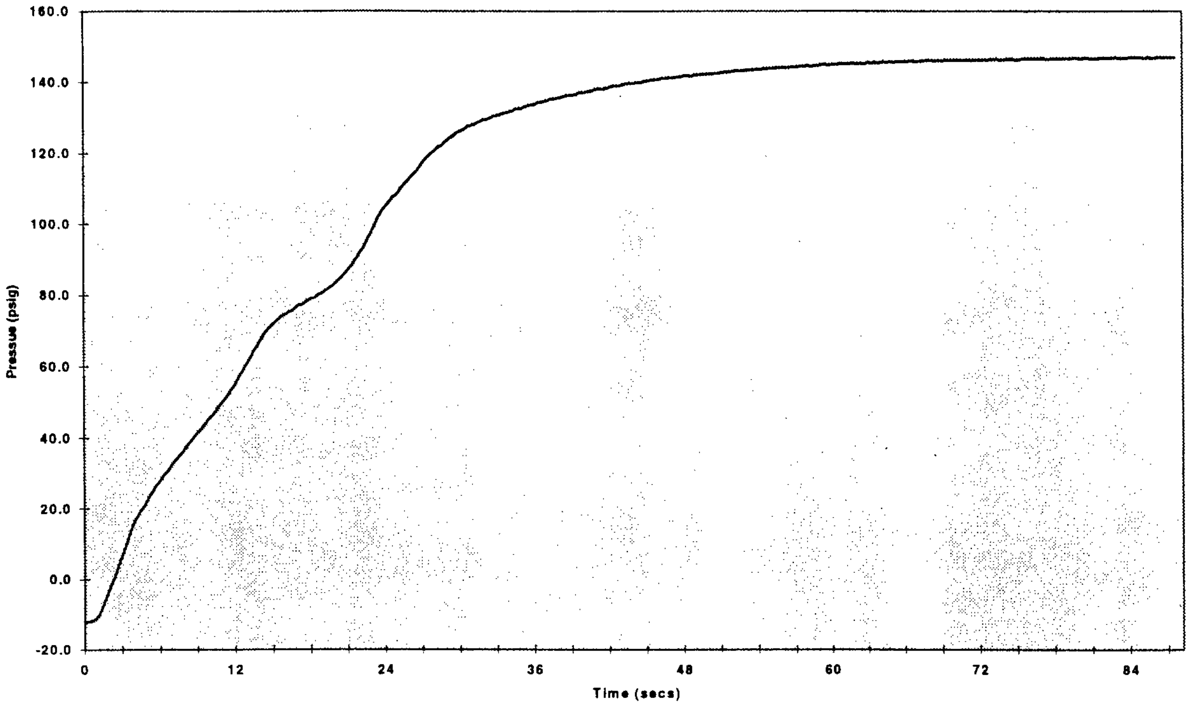


**Figure 4.** Pressure Response from First Cartridge Ignition - Dual Cartridge Demonstration

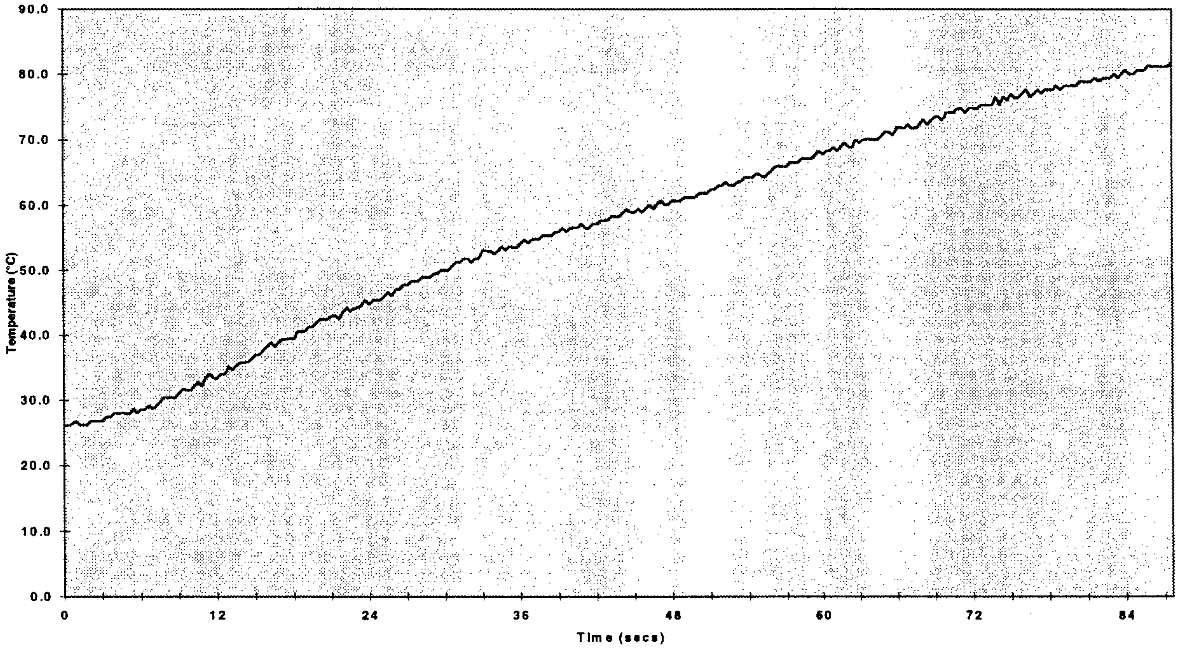


**Figure 5**. Temperature Response from First Cartridge - Dual Cartridge Demonstration

occurring in 84 seconds. The temperature, however, only rose from 57°C to 70°C. The heat capacity of the hydrogen present from the first cartridge firing appears to be responsible for the reduction in the magnitude of the observed temperature increase.

The pressure and temperature rise created by the second cartridge ignition is shown in Figures 6 and 7 respectively. The amount of hydrogen generated in each of the firing (based on 1.3 liters of generator volume and final pressure and temperature) was 12 liters (first cartridge) and 10.5 liters (second cartridge). These tests confirmed the earlier tests conducted in Russia, and indicated good reproducibility of results.

In August, tests were conducted to assess the safety of the dry dehydriding process. A particular concern was the possible structural and heat effects on the generator of initiating the SS reaction in the presence of air. Soldier safety requires determination of the consequences of fabrication failures.

A dry dehydriding hydrogen generator based on thermal decomposition of aluminum hydride is envisioned to consist of a replaceable magazine containing several hydride cartridges which will be fired one at a time as needed by the fuel cell hydrogen demand. The magazine will also provide a small reservoir volume. The magazines with cartridges are expected to be prefabricated for quick loading in a portable power package.

To provide undiluted, high-purity hydrogen for the fuel cell, the magazines will be evacuated and sealed with a check valve. The check valve will remain closed with vacuum conditions within the magazine, and will allow flow of hydrogen out of the magazine as it becomes pressurized by hydrogen production. The hydrogen flow rate will be controlled by a pressure regulator to provide a downstream pressure equal to the fuel cell operating pressure. The hydrogen flow rate will then be determined by the fuel cell demand.

It is anticipated that some air will be introduced during removal of a spent magazine and loading of a fresh magazine. However, the air will be confined between the magazine and fuel cell. The loading mechanism will be designed in such a way that the loading process itself will purge out almost all of the air so introduced. The check valve and the loading arrangement will assure that hydrogen produced will not come in contact with oxygen in the presence of any hot areas within the magazine.

Given that air will be purged between the magazine and fuel, SS initiation in the presence of air requires that (a) a magazine was not wholly or completely evacuated during the fabrication process, but the magazine's structural integrity is preserved, or (b) a magazine developed a leak allowing air to enter the magazine. Prior to the experiment, an effort was made to predict the effect of ignition in the presence of air, based on knowledge of the SS reaction. Specifically:

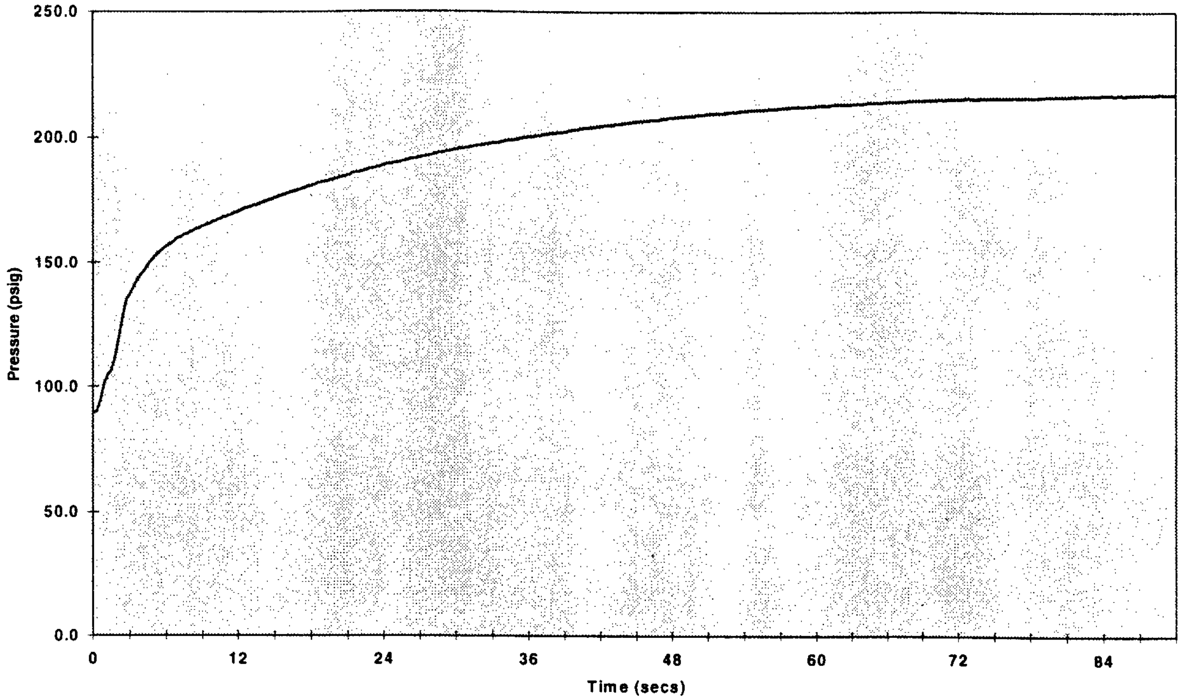


**Figure 6.** Pressure Response from Second Cartridge Ignition - Dual Cartridge Demonstration

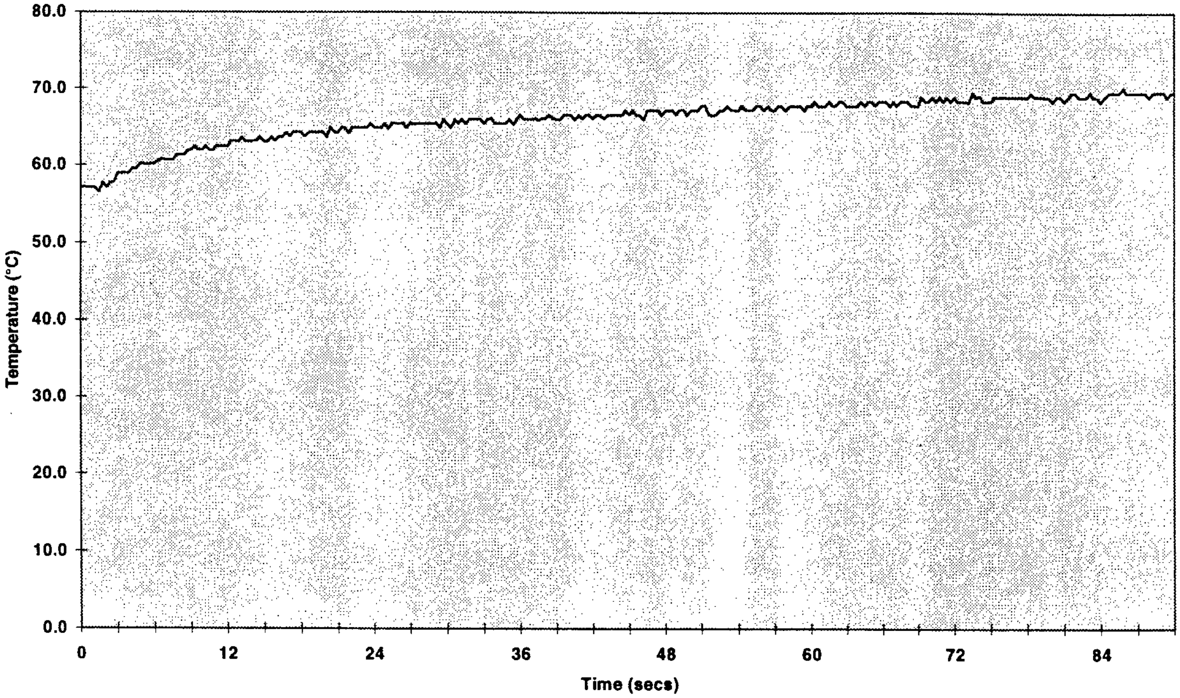


**Figure 7.** Temperature Response from Second Cartridge Ignition - Dual Cartridge Demonstration

- The dry dehydriding process is initiated by activating the Ti,B solid state reaction in the cylindrical cartridge core.

- The heat from the Ti,B reaction is propagated through the $AlH_3$-Ni active material by conduction.

- $AlH_3$ is decomposed thermally to produce hydrogen and metallic Al which reacts with Ni to form an alloy. While $AlH_3$ decomposition is endothermic, the alloy-forming reaction is exothermic and provides enough heat to produce an overall self-sustained (SS) reaction.

*Failure Scenario (a)*: Since the Ti-B reaction occurs first, hot surfaces will exist within the cartridge core before any hydrogen is produced. If any oxygen is present initially, it is expected to react rapidly with the first evolution of hydrogen over the hot areas until all available oxygen is consumed. This process itself is expected to prevent buildup of hydrogen in the presence of oxygen, so any violent reaction (implosion) is eliminated. The combustion of hydrogen does produce heat which will initially increase the rate of thermal decomposition of the $AlH_3$ charge. Therefore, the net results of firing a cartridge in scenario (a) will be (1) somewhat higher temperatures within generator due to the added heat of combustion of small part of hydrogen, and (2) loss of some hydrogen due to its combustion, with consequently lower pressure of hydrogen in the generator. Since buildup of hydrogen in the presence of oxygen is not expected to occur, firing a cartridge in air inside a sealed magazine will not lead to any explosion or a shock wave.

Assuming that:

- Generator volume = 1.3 liters
- One cartridge ($AlH_3$:Ni::1:1 by weight) = 24 g
- Equivalent hydrogen = 1.2 g = 13.4 liters at standard conditions
- Expected pressure rise = 10.3 atm
- Net heat generated by Ti-B and SS reaction= 7 Kcal

the expected increase in temperature and loss of hydrogen pressure (in the prototype generator, for example) can be estimated. If the generator is filled with air initially, it will contain 0.27 liters of oxygen which will consume 0.54 liters of hydrogen to produce 0.54 liters of water vapor. The water vapor is likely to react with Al to produce $Al(OH)_3$. The maximum amount of hydrogen produced is therefore 12.85 liters. The maximum expected pressure rise is (12.85-0.27)/1.3 = 9.7 atm, which is 6% lower than if the generator had been evacuated. If the formation of $Al(OH)_3$ interferes with the SS reaction or with heat conduction, the production hydrogen may be reduced to a greater extent. The combustion of 0.54 liters of hydrogen will add approximately 1.4 Kcal of heat which would be an increase of 20% in net heat produced (assuming complete dehydriding reaction as before) by the generator which should lead to corresponding increase in the gas temperature (about 10°C greater than firing in vacuum).

These calculations indicate that firing a cartridge in air will actually decrease pressure in the generator and will lead to a small increase in gas temperature. No explosion potential or shock wave phenomena are anticipated.

*Failure Scenario (b)*: The primary difference between this scenario and that described earlier is that a leaky magazine will not be able to hold hydrogen pressure. The initial sequence of events will be identical to that described for scenario (a) until all initial amount of oxygen in the magazine is exhausted by reaction with the hydrogen. No explosion potential and shock wave phenomena is anticipated up to this point as described before. As the subsequent hydrogen evolution increases pressure inside the magazine it will start leaking outside. Greater pressure within the magazine and generator will, however, prevent any ambient oxygen from entering the magazine, thus avoiding contact with hydrogen over the hot surfaces within the magazine. The leaking hydrogen will be much cooler and will be diluted by ambient air rapidly and no explosion hazard is anticipated. Hydrogen leakage is, of course, a potential problem with any hydrogen source design, but should be easily prevented.

In order to verify the predicted decrease in hydrogen pressure and modest increase in gas temperature, two experiments were conducted. In the first experiment, one $AlH_3$ cartridge was fired in vacuum in the prototype generator. In the second experiment, one cartridge was fired in the sealed generator without evacuation (i.e. in the presence of ambient air).

The first experiment was similar to RTI's previous demonstration experiments in July and produced final hydrogen pressure of 132 psig upon cooling the generator to ambient temperature. The net increase in hydrogen pressure was thus 146 psi. The second experiment simulated the failure scenario (a). No explosion or shock wave phenomena were observed, as indicated by an intact cartridge holder assembly inside the generator. The final hydrogen pressure was observed to be 105 psig, which also was the net increase in hydrogen pressure. Thus firing a cartridge in air resulted in almost 28% reduction in hydrogen pressure. Theoretical calculations described earlier predicted about 6% reduction with completion of the dehydriding reaction. The fact that the observed hydrogen pressure reduction is greater than 6% indicates the possibility that hydrogen combustion reduced the extent of subsequent dehydriding reaction.

The pressure rise patterns for both experiments are shown in Figure 3-5. The initial part of the pressure rise trace in the air firing experiment clearly showed a brief peak and dip in the gas pressure indicating the hydrogen combustion reaction. The initial slope of pressure rise in both cases was about the same in spite of the added heat of hydrogen combustion.

The peak gas temperature inside the generator under air firing conditions was about 89°C which appears to be somewhat lower than the vacuum firing case. The surface temperature of the generator in the evacuated generator demonstration was also about 89°C. The temperature of hydrogen itself leaving the generator will be much lower than that inside the generator due to high heat capacity of hydrogen and cooling in the plumbing lines.

The experiments clearly indicated that the $AlH_3$ cartridges can be fired in presence of air without explosion or shock wave hazard. The results indicate that hydrogen combustion has a quenching effect on the dehydriding reaction. This leads to lower hydrogen generation and increases safety

even further. The safety problem associated with hydride cartridge ignition in an air environment is minimal. Some retardation of reaction and hydrogen production may occur. This would occur only for the first hydride cartridge, since its hydrogen would consume all oxygen, purge the system, and ensure that all subsequent dehydriding takes place in a pure hydrogen environment.

## 3.3 Gas Chromatograph Analysis of Hydrogen Produced from $AlH_3$ in the SS Reaction.

The purity of hydrogen generated in tests conducted in Russia as determined by gas chromatographic analysis was over 99%. The hydrogen purity was confirmed in tests conducted at RTI with more detailed analysis of impurities. The generator was evacuated and backfilled with nitrogen three times before evacuating again. A gas sampling canister was also completely evacuated. The hydride cartridge was thus fired in vacuum conditions.

The sample canister was filled with the gas produced and the gas sample was analyzed without

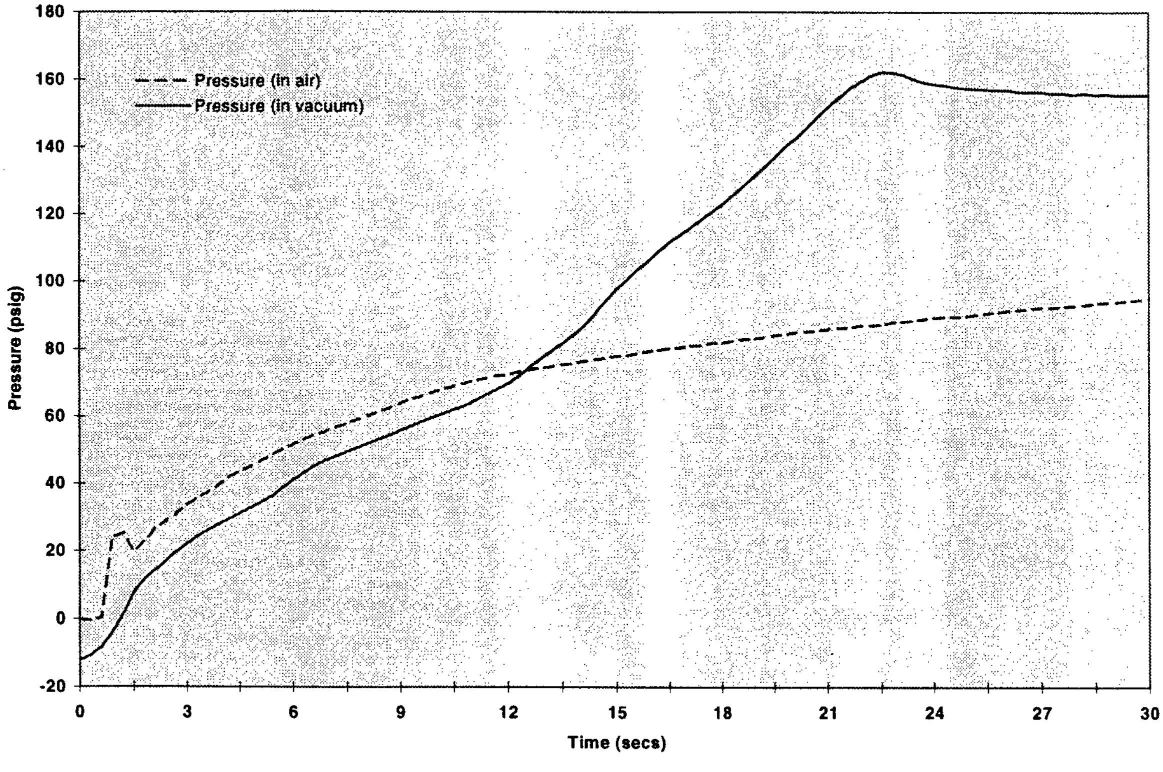
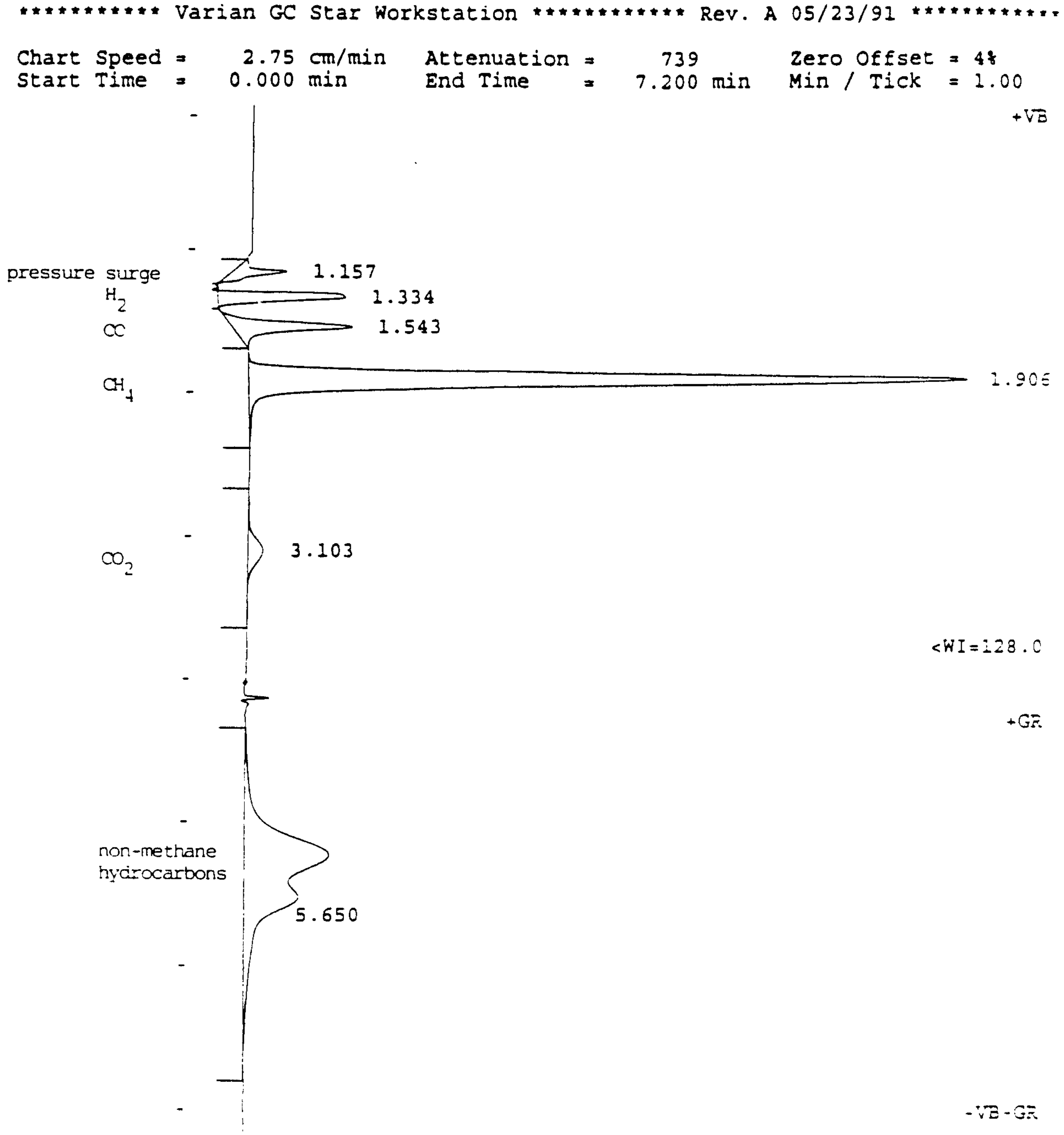


**Figure 8.** Pressure Response from Single Cartridge Ignition in Air and in Vacuum

dilution by a gas chromatograph calibrated to determine CO, $CO_2$, $CH_4$, and non-methane hydrocarbons. The combined impurities concentration was determined to be about 0.36%. The GC trace of the sample analysis is shown in Figure 9. The individual concentrations by volume were estimated to be: CO - 246 ppm, $CO_2$ - 89 ppm, $CH_4$ - 2,025 ppm, and non-methane hydrocarbons - 1,290 ppm. The purity of hydrogen produced was thus over 99.6%. The effect of measured impurities on fuel cell operation and the probable cause of the impurities is addressed further in Section 4.3.



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*********** Varian GC Star Workstation *********** Rev. A 05/23/91 ***********

Chart Speed =    2.75 cm/min    Attenuation =     739        Zero Offset = 4%
Start Time  =   0.000 min       End Time    =   7.200 min    Min / Tick  = 1.00
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**Figure 9.** Gas Chromatograph Analysis of Hydrogen Produced from Dry Dehydriding of $AlH_3$

## 4. Estimates of Technical Feasibility

The results obtained in this Phase I effort address the fundamental issues affecting the technical feasibility of the use of dry dehydriding for hydrogen production. Basic generator design is accomplished, and the required chemical and mechanical techniques for cartridge construction are understood and attainable. Issues relating to gas purity and generator safety have been addressed. The reaction rapidly produces adequate hydrogen on demand for small fuel cell use (0.56 standard liters per gram of $AlH_3$:Ni , mixed 1:1 by weight.)

Stability during storage was addressed by scientists at SSC-RF. In general, $AlH_3$ was found to be very stable when stored under dry conditions (relative humidity less than 50 to 60%) at temperatures below 20 °C in sealed plastic bags. The literature review confirmed the remarkable storage stability of $AlH_3$ when stored in dark for several months (Herley et al, 1981). The reaction of $AlH_3$ even in contact with liquid water has been found to be slow with less than 1% decomposition at ambient conditions.

An important feature of the dry dehydriding reaction which contributes greatly to its use is inherent attitude insensitivity. The absence of any liquid phase is responsible for this distinct advantage over hydrolytic reactions. All reagents and products are solid state.

Further efforts will refine the basic techniques and knowledge leading to a finished product - a safe, portable, and field rechargeable power pack. Complete technical feasibility requires that future work resolve issues revealed in Phase I testing. All of these issue are seen as easily resolvable with proper engineering design. Specifically, these issues are:

- Heat Dissipation
- Reaction By-product Dust Filtration
- Effects of Gas Contaminants on Fuel Cell Performance
- Reaction Safety in Air
- Ease of Handling

### 4.1 Heat Dissipation

For field use, a prototype device must be safe to handle. The laboratory tests indicated reactor surface temperatures of up to 80 °C immediately following the firing of the first cartridge. The temperature rise was found to be modest for subsequent cartridge firing in a warm hydrogen atmosphere. For a 300 W requirement the time lag of at least 5 minutes between successive cartridges is anticipated to cool the reactor surface significantly. However, the peak external surface temperature sensed by a soldier or other end user should be reduced below 60 °C. Two approaches will be used to reduce the surface temperature. First, methods to reduce the peak reactor temperature would be considered. Second, ways to improve heat dissipation would be investigated. In the first approach, the choice of alloying metals (M) and the minimum required ratio of $M:AlH_3$ for self-sustainability will be investigated further to minimize the net heat generated during hydrogen generation. Alternative cartridge geometries will be investigated to slow down the hydrogen generation reaction and consequently the peak reactor temperature. In the second approach, shallow fins or ridges will be used with insulating material edges on the outer surface of the reactor to reduce the temperature sensed by a soldier as well as to promote cooling of the reactor body.

### 4.2 Reaction By-product Dust Filtration

For efficient fuel cell operation, the hydrogen supply must be free of particulate matter to prevent deposition in narrow fuel cell gas flow channels. Although gaseous hydrogen is the primary product of the dry dehydriding process, some solid particles are generated due to the rapid, high-temperature Ti,B initiation and the SS reaction. High efficiency glass fiber filter material on the perforated cartridge ends will prevent particulate emissions. Additionally, a high efficiency in-line filter will be installed in the tubing connecting hydrogen generator to the fuel cell.

### 4.3 Effects of Gas Contaminants on Fuel Cell Performance

As discussed in Section 3.3, the primary impurities found in hydrogen were CO, $CO_2$, $CH_4$, and non-methane hydrocarbons. Only CO, which was found to be of the order of 250 ppm, would be potentially detrimental. The platinum based electrocatalysts used in PEM fuel cells are poisoned by even small traces of CO, which must be reduced below 10 ppm. The source of oxygen for CO formation is likely to be any solvent or binder materials used in the preparation of the $AlH_3$ cartridges and Ti-B cores (e.g. polyvinyl alcohol was used as a binder in preparation of Ti-B cores). In fact, all CO and $CO_2$ present in the chromatographic analysis can be accounted for if only 25% of the polyvinyl alcohol Ti,B binder contributed oxygen to side reactions upon thermal decomposition. Alternative oxygen free solvents (e.g. heptane) and binder materials (e.g. Teflon) would therefore be investigated to eliminate any source of oxygen for CO formation. Another source of oxygen could be incomplete evacuation of the generator or any small amount of air leak. For such situation, the CO will be present only for the first cartridge firing since all subsequent firings would be in hydrogen atmosphere. In such a case, it would be possible to vent the hydrogen generated by the first cartridge, and utilize only the hydrogen produced by subsequent cartridges in the fuel cell.

### 4.4 Reaction Safety in Air

The safety issue concerning hydrogen-oxygen reaction over hot generator surfaces was experimentally addressed in the experiments conducted at RTI as described in Section 3. A hydrogen cartridge was fired in the presence of ambient air sealed in the generator. The experiment indicated a safe operation. The presence of air in the generator, however, is not desirable from contamination point of view. Any oxygen present reduces the hydrogen output of the generator. Secondly, it also increases the chances of CO formation which would be a concern for fuel cell operation. As discussed earlier, the cartridge magazine will be fabricated in vacuum with a vacuum seal indicator. The magazine loading process will be designed so that the loading process itself will flush out any air present in the connecting tubing.

## 4.5 Ease of Handling

Ease of handling to facilitate rapid reloading of a portable power pack depends on generator and magazine design. Generator design will revolve around magazine design, since the magazines will be evacuated and self-contained. The generator will consist of a shell which accepts the magazine, the necessary fittings for connection to the fuel cell, and electronics for controlling cartridge ignition.

The cartridges can fit into a cylindrical magazine filled with a "honeycomb" structure. The size and number of cells in the structure can be controlled to tailor the magazines to varying power requirements. An end view of such a magazine might appear as in Figure 10.

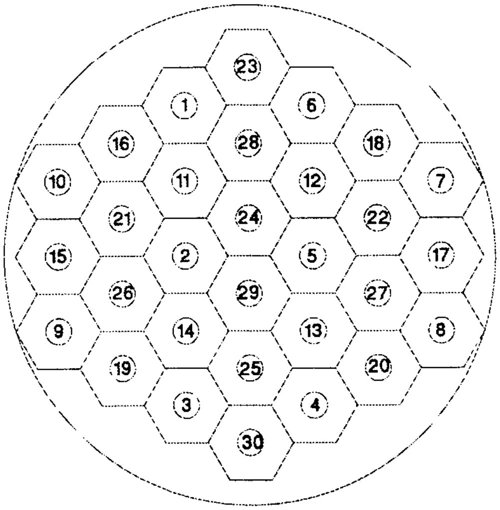

**Figure 10:** Cartridge Magazine -- End View

The magazine will be loaded into the generator so that the magazine contacts a plate with electrical contact which match conductive elements embedded in the magazine. Each conductive element corresponds to a cartridge. There are several methods by which initial energy application can be achieved. A rechargeable battery can heat a resistive element (e.g., nichrome wire) in contact with the cartridge surface or the battery might fire a tiny explosive (a squib)or ignite heat paper. Heat paper can also be ignited by friction or impact and has been used to start thermal batteries. A piezoelectric element like that used on many gas appliances will produce a voltage potential when mechanically stressed.

Once hydrogen production has begun, the ignition of the remaining capsules can be directed by electronic hardware powered by the fuel cell or backup battery. The decision to ignite a capsule will be made by a microcontroller responding to a low hydrogen pressure threshold. An electronic control scheme is illustrated in Figure 11. The simple pressure transducer is monitored by the microprocessor, which also chooses a cartridge location in the cartridge magazine by using the output of the decoding logic to select a driver to be fired. The selected driver output goes high, causing a voltage to be applied to the nichrome contacting the capsule. The microcontroller and interface circuitry must be able to withstand the field environment. Decoding logic and drivers are commercially available that meet military specifications. A microprocessor that will perform the required task and meet military temperature specifications is the Intel 8XC196NT/Q833. Electronics will be designed to have the least possible drain on the fuel cell.

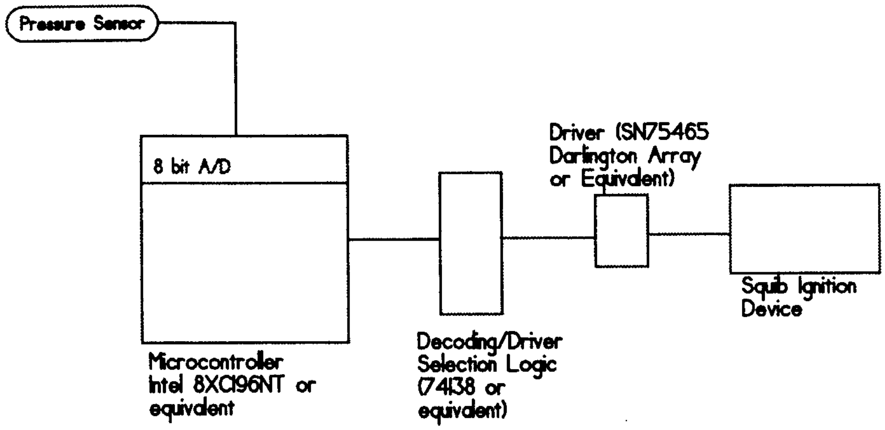

**Figure 11:** Control Circuit Block Diagram

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