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1. PROJECT OBJECTIVES

The objectives of this project were to (1) demonstrate the feasibility of a high-energy density, portable hydrogen source using metal hydride hydrolysis, and (2) provide the data required to design a system for controlled electrical power output. Both of these objectives were addressed in support of the development of a safe, efficient, quiet power source. The target for power output was 200 W (2ℓ/min of hydrogen), assuming an 800 Wh fuel pack.

Meeting the objectives required that several criteria for hydrogen production be addressed. First, the production of hydrogen per unit mass of metal hydride must be sufficiently high. Second, the purity of the hydrogen gas must meet minimum standards for fuel cell use. Third, the power source must be safe. This meant that heat from the exothermic reaction of water and the hydride must be dispersed. Fourth, the power source must be easy to use. These objectives were accomplished in different facets of the project, including fuel selection, hydrogen generator design, and fuel synthesis.

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2. WORK PERFORMED

In pursuit of the objectives described in section 1, the research team broke the project into tasks designed to answer questions of safety, hydride energy density, optimum fuel geometry, and cost effectiveness of various hydrides. Having answered these questions, a generator was designed to use the best hydride, which was identified as sodium aluminum hydride (NaAlH₄). This generator was tested in the laboratories of Research Triangle Institute in February of 1997.

2.1 Metal Hydrides - Selecting a Hydride Hydrogen Source

Prior to the commencement of the project, it was proposed that only magnesium hydride (MgH₂) and aluminum hydride (AlH₃) be considered as reaction candidates. This choice was based on an analysis of several different hydrides. A hydride was sought which had desirable energy per unit mass for the goal of 200 W of nominal power production. Additionally, it was desirable to minimize toxic by-products, waste heat, and ensure a safe and controllable reaction. Costs of the hydride in terms of raw material, manufacture and storage requirements were also considered.

Table 1 lists some of the best reactive metals and metal hydrides for hydrogen production by water reaction and their reaction stoichiometry. In the table, Q_c is the combustion potential energy or higher heating value of the hydrogen per unit mass of metal or hydride, and Q_r is the heat released from the exothermic reactions with water, per unit mass of metal or hydride. In the absence of other factors, it is desirable to maximize Q_c and the ratio Q_c/Q_r.

Table 1. Hydride Reactions

Material	Reaction	Q _r MJ/kg	Q _c MJ/kg	Q _c /Q _r
Li LiH	2Li + 2H ₂ O → 2LiOH + H ₂ LiH + H ₂ O → LiOH + H ₂	28.4 15.6	34.2 30.0	1.2 1.9
Mg MgH ₂	Mg + 2H ₂ O → Mg(OH) ₂ + H ₂ MgH ₂ + 2H ₂ O → Mg(OH) ₂ + 2H ₂	14.5 10.7	9.9 18.5	0.7 1.7
Al AlH ₃	Al + 2H ₂ O → 2Al(OH) ₃ + 3H ₂ AlH ₃ + 3H ₂ O → Al(OH) ₃ + 3H ₂	4.7 3.9	13.3 24.0	2.8 6.2
LiAlH ₄	LiAlH ₄ + 4H ₂ O → LiOH + Al(OH) ₃ + 4H ₂	5.5	25.3	4.6
NaBH ₄	NaBH ₄ + 4H ₂ O → H ₃ BO ₃ + NaOH + 4H ₂	4.4-17.1*	25.5	1.5-5.8*
NaAlH ₄	NaAlH ₄ + 4H ₂ O → NaOH + Al(OH) ₃ + 4H ₂	8.2	21.2	2.6

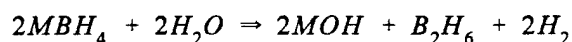
* catalyst dependent

There are obvious differences among the various hydrides. In choosing magnesium hydride as a starting point, motivation was provided by several characteristics exhibited by magnesium. Magnesium is readily available, has low cost, long and stable shelf life, controllable reactivity, and benign byproducts. Also, it is a metal with which the research team had considerable past and recent experience, including demonstrating the acceptable behavior of the metal in military-related applications. However aluminum is also inexpensive and plentiful and is a metal that the research team has investigated for hydrogen production.

In the course of the project, other metal hydrides were investigated. They include, besides those in Table 1, lithium boron hydride (LiBH_4), lithium aluminum hydride (LiAlH_4), beryllium hydride (BeH_2), beryllium boron hydride ($\text{Be}(\text{BH}_4)_2$), sodium hydride (NaH), calcium hydride (CaH_2), and aluminum boron hydride ($\text{Al}(\text{BH}_4)_3$).

Boron hydrides of lithium, beryllium, and aluminum have high energy densities. Beryllium hydrides in particular are nearly two and half times as efficient as NaAlH_4 or MgH_2 in production of hydrogen measured in liters per kilogram of hydride. However, each of these hydrides have drawbacks. Lithium is a rarer and more expensive metal than either magnesium or aluminum, and displays pronounced explosive reaction tendencies and poor stability characteristics. Hydrides containing beryllium have manufacturing and disposal problems, since beryllium is an extremely toxic metal.

Aluminum boron hydride is thermodynamically unstable and decomposes to form hydrogen even at normal conditions (room temperature and pressure). The compound is extremely reactive and is flammable even in media with only trace amounts of oxygen and moisture. Boron hydrides in general have another disadvantage, in that use of boron hydrides demands the presence of catalysts and also leads to hydrogen contamination by diborane, in accordance with the reaction:



where M is replaced by Li, Al, or Be. Diborane is a poisonous gas.

Other investigators have examined sodium boron hydride and proposed it as a hydrogen energy source for portable power packs (Bloomfield, 1995). Energy density for this hydride is good and the water requirement for hydrogen production is the same as for magnesium hydride. However, problems were encountered with water sorption and contacting and reaction control. Hydrate formation and masking of the reaction surface also caused problems. As with other boron hydrides, the NaBH_4 also requires catalysts. The catalysts are required to affect pH as well as promote reaction. If the correct pH (4-5) is not present, the reaction will slow down and/or not be driven to completion. The reaction rate also exhibits dependency on temperature.

An additional selection requirement was that the material be in a solid state. This facilitates ease of use and reduces weight and volume requirements. Liquid materials represent a storage

problem because of the possibility of leaks. Gaseous materials would have too low a density to avoid tanks with large volume, and hence large size. Under normal conditions, this left only seven candidate hydrides which had useful energy density. Of those, two were lithium hydride and lithium aluminum hydride. One compound was sodium boron hydride.

Sodium boron hydride has the drawbacks described previously. Lithium hydride, lithium aluminum hydride, and the fourth compound, calcium hydride, produce insoluble by-products. There is also no large-scale industrial production of lithium hydrides, as opposed to other hydrides. Research carried out in Russia showed that hydrolysis of lithium hydride and aluminum lithium hydride results in a surface coat of insoluble lithium hydroxide. This slows the speed of the reaction.

The remaining candidates were MgH_2 , AlH_3 , and $NaAlH_4$. Comparing these compounds, the ratio Q_c/Q_r was highest (6.2) for AlH_3 , followed by $NaAlH_4$ (2.6) and MgH_2 (1.7). In addition to its low value of Q_c/Q_r , magnesium requires a high activation energy.

The obvious choice would seem to be AlH_3 . $NaAlH_4$ however has certain advantages which outweigh its lower ratio of hydrogen energy to reaction heat energy. Those advantages are:

- Stable storage - Aluminum hydride can have explosive tendencies when stored and is often used as a propellant. By contrast, $NaAlH_4$ is easily storable at standard temperature and pressure, requiring no special storage conditions. However, it is preferable to seal it from air in plastic bags or similar inexpensive containers, since at 60% relative humidity and $20^\circ C$, a 35 gram, unprotected block of $NaAlH_4$ can lose about 5% of its mass in one day.
- Cost and availability - $NaAlH_4$ is in industrial scale production in Russia. Consequently, it was less costly to obtain. This hydride was readily available to team members in Russia. A one-time cost offered by the State Scientific Center in Russia, including manufacture and shipping, was \$200.00 per kilogram. This cost could be reduced by at least an order of magnitude for high-volume production.
- Soluble byproducts - When mixed with approximately 10% NaOH and NaH by weight, $NaAlH_4$ produces soluble byproducts in excess water. In contrast, the byproduct of the pure sodium aluminum hydride and of AlH_3 is $Al(OH)_3$, which is insoluble in water. The solubility of the byproduct facilitates handling and ease of use, reducing the effort required to remove byproduct from the generator. The solubility of the byproducts also ensures that coating of the hydride surface with inhibiting effects does not take place during the reaction.
- Neutral reaction media - $NaAlH_4$ will react with water which is neutral in pH, as well as with liquids which are not. However, AlH_3 does not react noticeably in pH neutral media, decomposing only 1% in more than an hour at $40^\circ C$. Acids can be used, but

inorganic acids such as H_2SO_4 , HNO_3 , and H_3PO_4 cause reduction of anions which results in the formation of SO_2 , NO , and other gases. This causes hydrogen contamination.

- Wide range of reaction temperature - NaAlH_4 can be made to react at temperatures in the range of -40°C to 40°C .
- Fast shut-down and start-up time - Upon contact with water or removal of water from surface contact, hydrogen production increases or decreases within 2-3 seconds (only seconds were required to reach nominal hydrogen production in our own generator tests).
- Pure hydrogen - A method has been developed whereby NaAlH_4 can be created without the use of organic solvents. Hydrogen fuels which are created with organic solvents may have ppm traces of CO_2 and possibly CO . In the United States organic contaminants, such as polyethers, are also a problem with synthesis of hydrides such as AlH_3 . Alkaline electrolyte reactions with CO_2 in fuel cells can result in the precipitation of insoluble carbonates. However, even with production using organic solvents, this hydride has been used in fuel cells for various applications in Russia without contamination of the fuel cell. This was another concern relative to NaBH_4 , which uses epoxy binders. The potential for the epoxy binder to pass through to the fuel cell and poison its operation has not been thoroughly examined.

It was desirable to minimize the dispersion of heat from the exothermic reaction associated with dehydriding. This factor was examined for each of the hydrides mentioned above. Table 2 shows the heat produced in kJ/mol of some of the hydrides examined, as well as for the hydrolysis of pure metals.

For different hydrides, the reaction heat produced per mole of hydride varies widely. However, the moles of H_2 produced per mole of hydride or metal varies widely as well. When the heat produced by hydrolysis is considered on a basis of kJ per mole of H_2 produced, the heat production is seen for all hydrides, with the exception of NaH , to fall in the range of 110-140 kJ/mol H_2 . Those hydrides which produce the most heat per mole of hydride also produce more hydrogen gas. Hydrides which have sufficient production of H_2 in ℓ/min to meet energy requirements produce more heat than hydrides which cannot meet the production requirement with a reasonable mass of the hydride. Clearly, the hydrides as group are favored over pure metal reactions in the amount of heat produced per mole of H_2 .

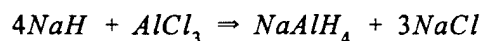
2.2 Properties and Characterization of Sodium Aluminum Hydride (NaAlH_4)

As mentioned previously, NaAlH_4 is in commercial production in Russia. The most widespread technology for the synthesis of NaAlH_4 is an exchange reaction which takes place in the presence of the organic solvent tetrahydrofuran (tetramethylene oxide).

Table 2. Heat Production (kJ/mol) in Hydrolysis of Select Hydrides

Substance	kJ/mol hydride	kJ/mol H ₂
LiH	108.2	108.2
LiAlH ₂	510.0	127.5
NaH	83.3	83.3
NaAlH ₄	444.6	111.2
MgH ₂	273.0	136.5
AlH ₃	407.0	136.0
CaH ₂	223.6	111.8
Mg	352.7	352.7
Al	436.0	290.7

The reaction is



The sodium chloride is filtered from the end-product. The filtrate, NaAlH₄, is mixed with toluene, then warmed to between 103°C and 110°C. In this process, any tetrahydrofuran is consumed in the toluene, which is in excess. This process produces crystalline NaAlH₄, which is not soluble in toluene. To produce an end-product free from organic impurities, the crystalline mass is washed in ether through a special filter. After this process is complete, the resulting suspension (NaAlH₄ in ether/toluene mixture) is dried of ether (boiling point 34°C). What remains are crystals of NaAlH₄ in toluene. The toluene is then separated from the crystals under vacuum. The resulting product must be stored in an inert atmosphere such as nitrogen.

Scientists at the State Scientific Center of the Russian Federation have developed an alternative, proprietary method of preparing NaAlH₄. In this method, the compound is synthesized directly from the elements at high temperature and pressure. This method is more cost-effective than the synthesis with organic solvents described above. Because of the absence of organic solvents, the production of contaminate-free hydrogen is assured.

Initial work on hydrolysis of hydrides by the project team had focused on small capsules of hydrides, referred to as microcapsules. Concepts for hydride encapsulation have been discussed in the recent literature (Ward, 1993; Akiyama, 1995; Shirvinsky, 1996). The microcapsules would be placed in a "macrocapsule" containing water as shown in Figure 1. The microcapsules were envisioned as having an electrically conductive coating. In the presence of water, a path is

provided for micro-arcing between capsules. The resulting generated heat removes the coating on the microcapsules, allowing hydrolysis to take place between the water and hydride. The macrocapsule would become a "charge" in a generator.

While it was possible to obtain microcapsules of the hydride with relative ease, on examination the technical barriers to developing the macrocapsule and then testing to establish reliability and safety were deemed too high to address in the Phase I effort. Because the microcapsules require an initial energy input to react, an investment in electrical and electronic hardware is required. Research and calculation showed that the additional weight of hardware required to ignite the microcapsules had a significant negative impact on the total system weight.

Russian team members Nikolai Efimov and Pavel Storozhenko proposed an alternative using NaAlH_4 in the form of pellets which would dehydride upon contact with water. They had already established familiarity with this technology through previous work. Use of the technology allowed concentration on generator design and control rather than on development of charge containment.

To create pellets of NaAlH_4 for hydrolysis, the compound is produced by one of the methods previously described. The resulting crystalline hydride is powdered in an inert atmosphere.

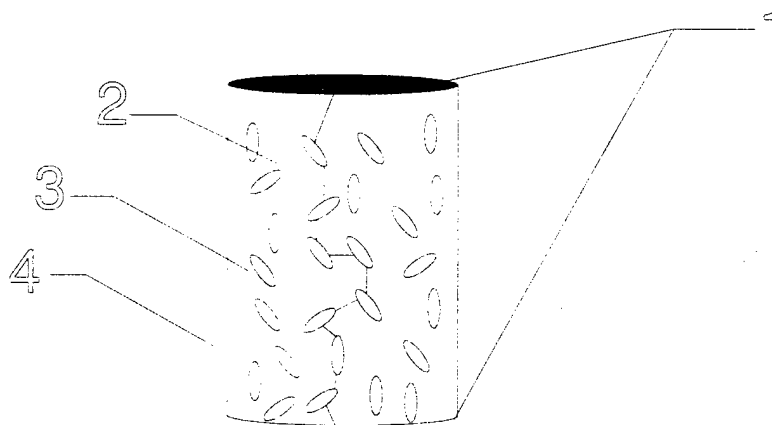


Figure 1: Microencapsulation. (1) metal electrodes (2) breakdown current path (3) microcapsule (4) macrocapsule

While remaining in the inert atmosphere, the powdered hydride is mixed with the additives NaOH and NaH which provide byproduct solubility. This mixture, still in inert atmosphere, is pressed into pellets with a pressure of approximately 1000 kg/cm² (14,000 psi).

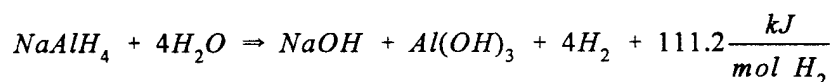
The production of the pellets in inert atmosphere prevents premature loss of product and provides controlled conditions for fabrication. However, the pressed hydride is relatively stable under normal conditions. As noted earlier, simple storage in sealed plastic will suffice for long term shelf life. The small amount of moisture in air trapped in the sealed plastic will react with the hydride to a very small extent. Reactivity and material loss ceases. If the hydride is packaged in an inert atmosphere, even this negligible loss can be avoided.

The high pressure production of the pellets is an important factor in the rate of dehydriding. A pellet which is made at insufficient pressure will be porous. Since the rate of the reaction of any hydride is a function of the surface area exposed to water, porosity will multiply the exposed surface area, leading to a higher rate of hydrogen production. This effect can be used to advantage as a form of coarse control of hydrogen production rates. It is also a factor in the fine control of hydrogen production.

Control of hydrogen production from hydrolysis with any complex or simple hydride or active metal requires control of the amount of surface area of the hydride/metal which is in contact with water. For the microencapsulation scheme, this control might have been accomplished by controlling the thickness of the conductive material coating on the microcapsules. Another possible approach was the production of blocks with predefined channels. The number and size of the channels would control the rate of reaction by defining the available surface area at any point in the reaction. Clearly, if the surface area exposed to water at any point in the reaction is a constant, the rate of hydrogen production will be constant.

This factor was taken into account in the choice of fuel geometry. Based on the reasoning that a cylinder being consumed at the same rate from all sides would maintain constant surface area throughout the reaction, cylindrical pellets of pressed NaAlH₄ were used as a fuel source (see Figure 2).

The chemical equation



is not a complete characterization of the reaction of hydrolysis of sodium aluminum hydride. Additional hydrolysis occurs with NaH. However, the mass/energy balance for the reaction can be closely approximated from this equation (see section 2.3 Generator Design and Construction).

Reaction speed and production of H_2 can be controlled by regulating the mass of the reactants. Process control in other generators (Bloomfield, 1995; Alexander, 1996) has been achieved by altering the amount of water available to the reaction. However, the rate of production of H_2 requires that a receiver or accumulator be used to provide a consistent level of H_2 for fuel cell consumption. The use of pressed hydride pellets with low porosity means that the reaction takes place only on the surface of the pellet, and greatly reduces the kinetics of the reaction. As soon as water is removed from the surface, the reaction will cease.

It is possible to achieve hydrolysis of $NaAlH_4$ below $0^\circ C$ using a salt solution. Russian tests have proven operation below $-20^\circ C$ using antifreeze solutions.

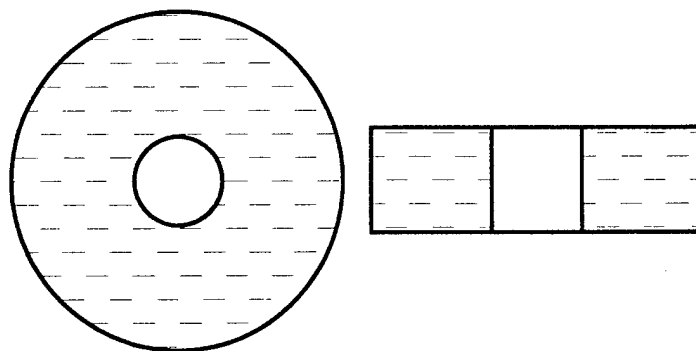


Figure 2: Hydride Pellets - Top and Side Views

2.3 Generator Design and Construction.

Having determined the characteristics of the hydride to be used, the research team designed a generator to utilize the tablets of pressed aluminum hydride. The design was driven by

- need for controllable production
- ease of recharging
- ease of cleaning
- minimum volume of package
- heat dispersion

Minimum weight will ultimately be an important consideration, but to maintain emphasis on functionality this factor was not completely treated in Phase I.

The objective was a generator which could produce a nominal 200 W of power and 800 Wh of energy. Defined ranges of operation were for 500 W of power over a period of 15 minutes to 50 W over a period of 4 hours. The generator designed in Phase I meets or exceeds those specifications.

The equation governing the hydrogen produced by the hydrolysis of NaAlH_4 (see above), the molecular weight of NaAlH_4 is 54.002 g/gmol, approximated as 54 g/gmol. A mole of sodium aluminum hydride will produce 8 g of H_2 . Figure 3 shows the relationship between various measures of hydrogen production and the power output of a 50% efficient fuel cell. Eight grams of H_2 is equivalent to 89.6 l of hydrogen at 11.2 l/g. The average weight of a pressed pellet of NaAlH_4 is 35 g. Since the pellets consist of 90% hydride and 10% NaOH and NaH , a pellet averages 31.5 g of NaAlH_4 , producing 53.1 l of H_2 . 800 Wh of fuel energy requires 226.8 l of H_2 , or about 4 pellets.

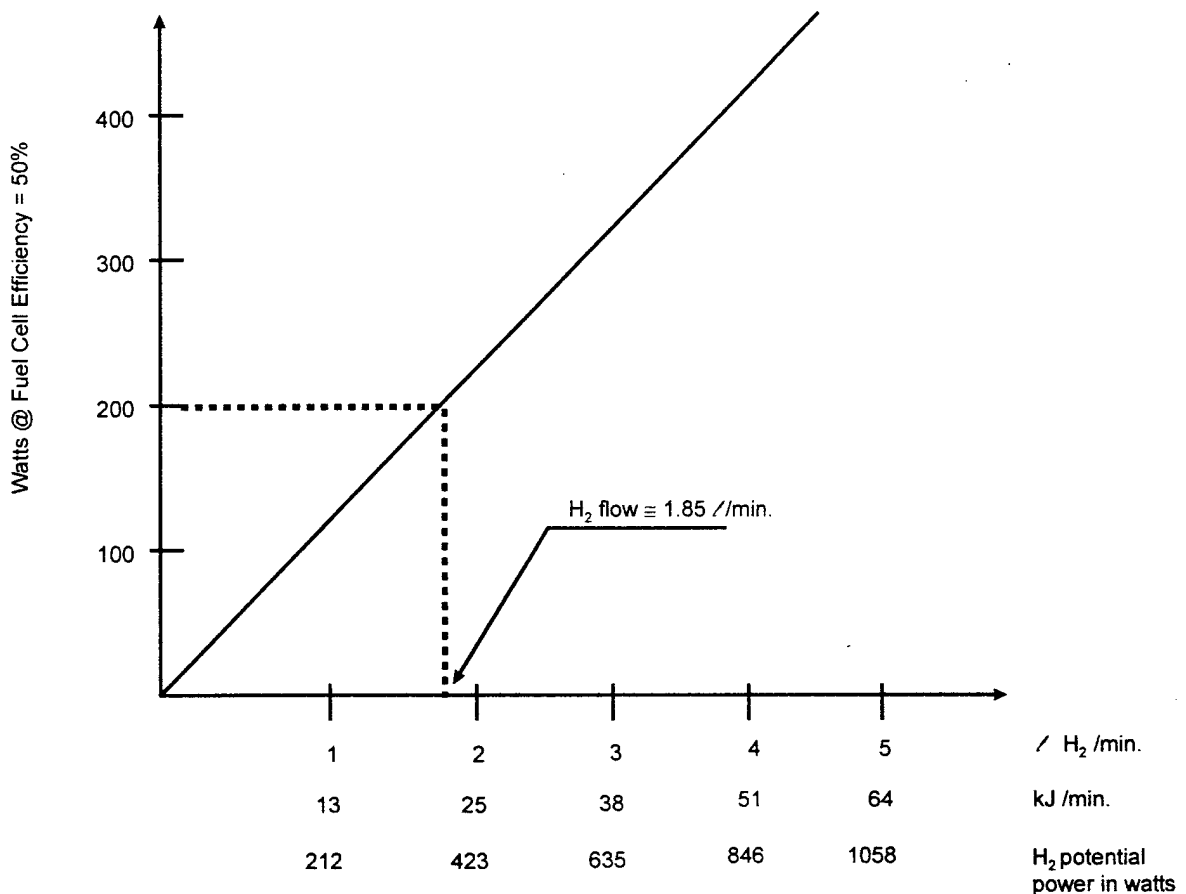


Figure 3: Power Output of a 50% Efficient Fuel Cell for Varying Hydrogen Gas Production Rates

From the stoichiometry of the reaction, 72 grams of water are required for each mole of hydride, 1.33 grams of water per gram of hydride, or approximately 180 grams of water for 4 pellets. To achieve full solubility of the byproducts, 2-3 times stoichiometric water is needed. We have used in Phase I four times stoichiometric water. The generator design was based on possible testing with up to 750 ml of H₂O.

From Table 2, a mole of NaAlH₄ will produce 444.6 kJ of heat energy. Each pellet represents approximately 0.58 moles, which is equivalent to 259.4 kJ of heat energy. Four tablets produce nearly 1040 kJ of heat energy. Nominal power production of 200 W will produce about 10 kJ per minute (2.4 kcal/min) of heat in the reaction zone. This heat can be dispersed by convective cooling.

These were the major physical factors considered in the design of the generator. The other issue was controllability. Since the control of the reaction was predicated on controlling water contact with the block surface, the design of the generator was also driven by how to achieve this goal and produce a fast-response reaction with a stable, easily controlled output.

Initial research was performed with a small generator which had previously been used to provide about 20 W of output power. This generator was used to model heat transfer and predict minimum water use. The final design for a nominal 200 W unit is shown in Figure 4. This batch generator has better heat transfer than the 20 W unit. Perforated fins allowed convective cooling.

The figure shows a cross-section of the generator. The generator consists of two parts: the cylindrical body (1) and a concentric inner cylinder (3). The body of the generator has a threaded lid (11) which is fitted with tubes for water input (7) and hydrogen gas exit (4). The water inlet tube shown in this drawing is somewhat altered in the as-built model, with the water inlet tube (7) actually penetrating the threaded lid (5). The gas exit tube (4) penetrates the threaded lid and continues through to connect with the inner cylinder. Hydride pellets (8) fit inside the inner cylinder and are held in place by an easily removable support (9). At regular intervals around the body, perforated copper fins (2) are soldered. The design calls for a gasket (6) between the generator lid and the body. The as built unit does not utilize this gasket.

The generator design is intended to create controllable hydrogen production. As the pellets of NaAlH₄ begin to react with water added to the generator, H₂ gas is produced and exits through the central tube (4). The amount of water in contact with the surface of the hydride becomes a function of the difference in the pressure due to the height of the water surrounding the inner cylinder and the pressure of the hydrogen gas produced.

When a valve is inserted into the gas exit line, the production of H₂ can be controlled by regulating the valve orifice size. When the valve is fully open, water will continue to contact the hydride surface to the level allowed by the amount of water added to the main cylinder. If the valve is closed to some degree, a pressure drop occurs across the valve and pressure begins to

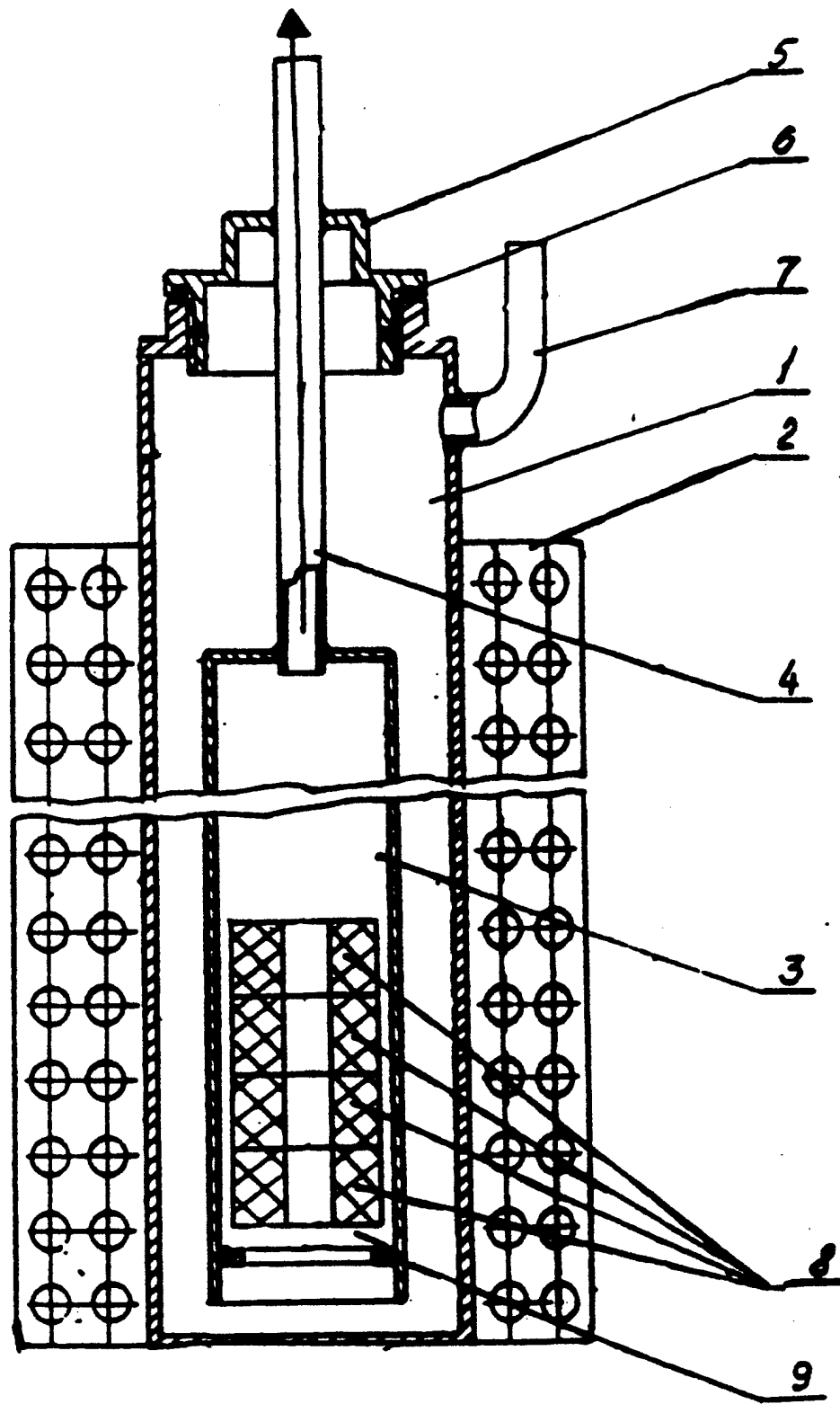


Figure 4: Reactor Components - (1) cylindrical body (2) cooling fins (3) inner cylinder (4) gas exit tube (5) threaded lid (6) gasket (7) water inlet tube (8) hydride pellets (9) pellet support

increase inside the inner cylinder of the generator. The increase in pressure forces water away from the hydride. When the pressure is sufficiently high to prevent contact between the water and the hydride, the reaction ceases. Thus closing the valve will terminate the reaction. The time from changing the valve position to altering the speed of the reaction is about 2-3 seconds. This is the contribution of the low-porosity pressed pellets. Water cannot reside in open channels in the pellets and allow the reaction to continue after the closure of the regulating valve.

3. RESEARCH RESULTS

Tests were performed with the generator design both at the State Scientific Center of the Russian Federation in Moscow and at Research Triangle Institute in the United States. Tests were performed to observe the controllability of hydrogen production, the maximum and minimum flow rates of hydrogen over time, and to gauge the external heat produced by the reaction.

Dr. Valentin Serebrennicov of Magnic International Inc. visited Moscow in December 1996 to observe tests. An example of the results from this testing are shown in Figure 5, including the flow of hydrogen gas in ℓ/min , the pressure of the gas in the inner cylinder of the generator as $^{\circ}\text{H}_2\text{O}$, and the surface temperature of the generator, as measured at the cooling fins, in $^{\circ}\text{C}$. This test was performed with 4 pressed pellets of NaAlH_4 at a room temperature of 18°C , and with 700 ml of water added to the generator.

Hydrogen production starts rapidly as the valve is opening, then levels off at 4 ℓ/min according to the final valve setting. Production remains steady at 4 ℓ/min for 48 minutes, then begins to taper off. Hydrogen production does not drop below 2 ℓ/min until 70 minutes have passed. Average production of H_2 in this interval is 3.7 ℓ/min . This is equivalent to a steady power output of 400 W for a 50% efficient fuel cell. Pressure in the internal cylinder of the generator did not exceed 6.8 $^{\circ}\text{H}_2\text{O}$ (~ 0.25 psi) and was generally stable during steady hydrogen production.

During stable hydrogen production, the outer surface temperature climbed to 47°C over a time of 35 minutes. The temperature remained between 44.5°C and 47°C during the next 35 minutes of the test, beginning to taper off as hydrogen production dropped.

Subsequent tests were performed at Research Triangle Institute. Drs. Efimov and Storozhenko visited Research Triangle Institute to help conduct tests and to demonstrate the generator to Dr. Richard Paur of the Army Research Office.

One test is illustrated in Figure 6 with a single 35 gram hydride pellet. Hydrogen exiting through the control valve was channeled through a desiccator, then routed through a mass flowmeter. A surface mount thermocouple was attached to a cooling fin of the generator.

Gas production was held at 2 SLPM (215 W) for five minutes. At that time the valve was adjusted to a flow rate of 4.7 SLPM (~ 510 W) for 5 minutes, and readjusted to a flow rate of 2 SLPM. This condition was maintained until the hydride reaction began to exhaust itself at approximately 18 minutes. Considering only the time of significant hydrogen production (> 2 SLPM), the average value of production was 2.5 SLPM (270 W) for a period of 18 minutes.

The maximum surface temperature attained was 53.7°C . The byproduct was dissolved in the water after tests and the generator was easily cleaned

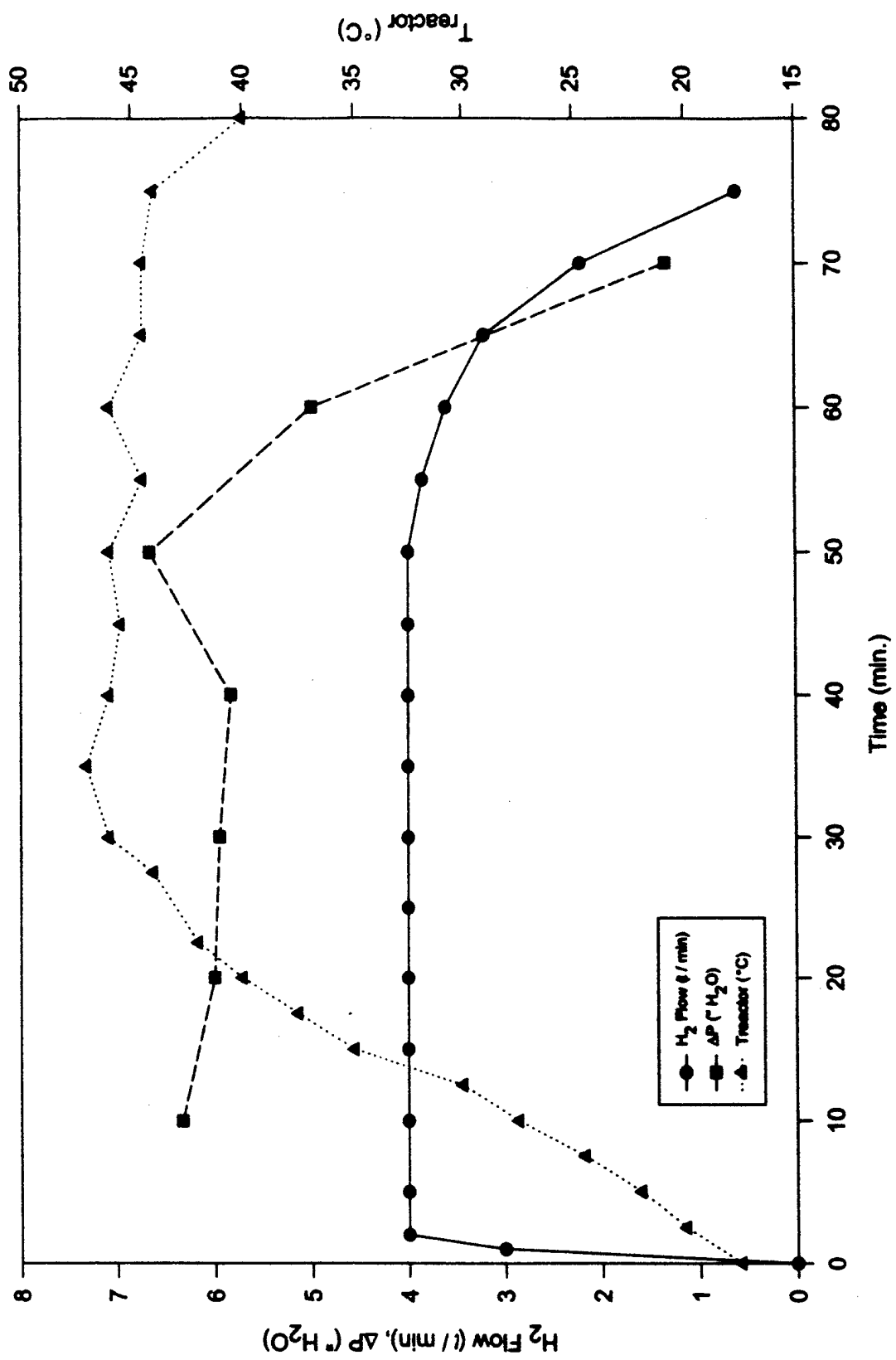


Figure 5. 4 blocks 700 ml H₂O, T = 18°C

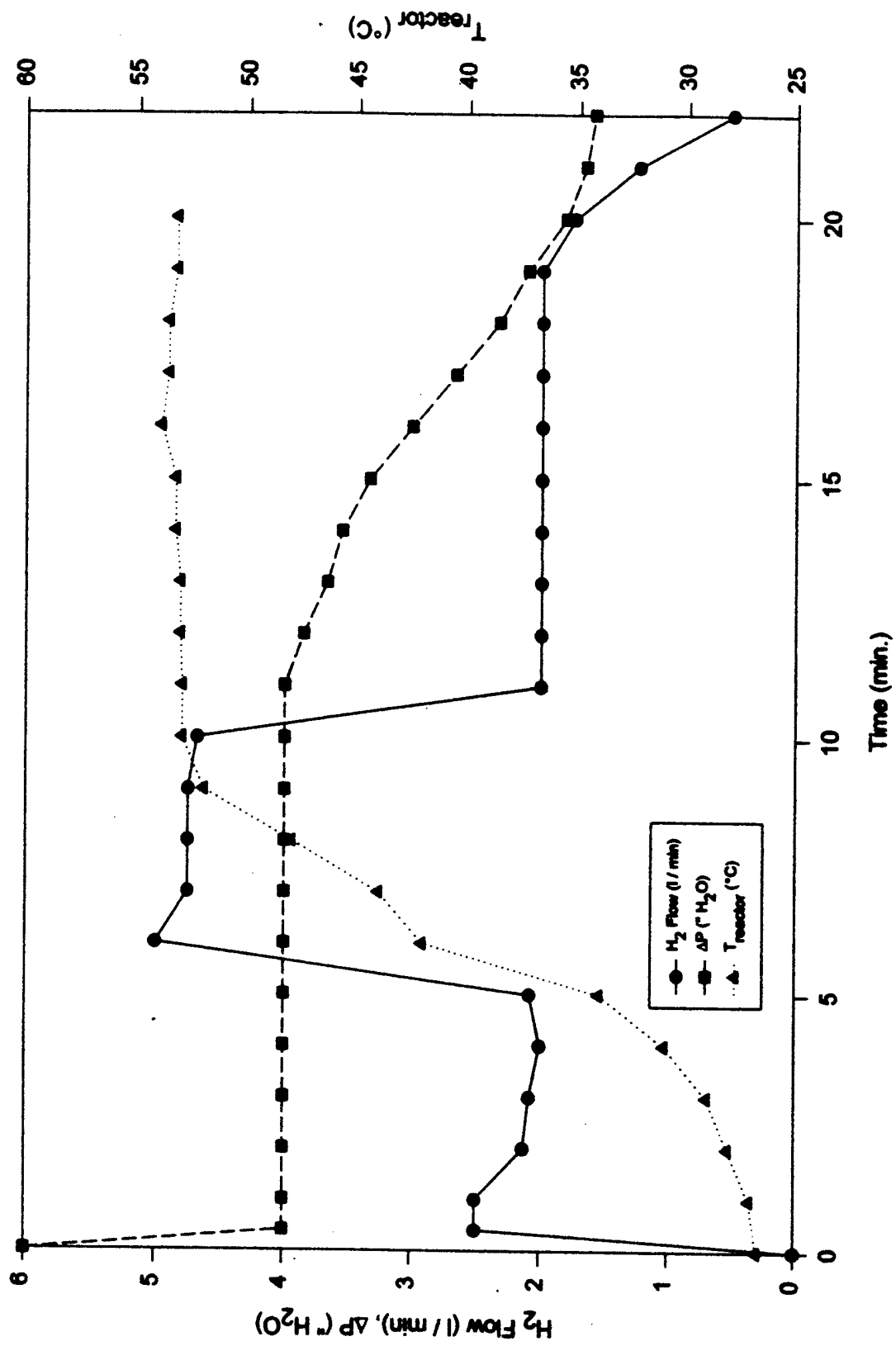


Figure 6. 1 block, 250 ml H₂O, T = 25° C

Results from another test with 2 pellets of hydride are shown in Figure 7. An average gas flow of 9.8 SLPM (~1.05 kW) was established for a period of 3 minutes, flow was reduced to an average value of 2.3 SLPM (~250 W) for a period of 17 minutes, and then readjusted to 9.5 SLPM (1.03 kW) for two minutes. Flow was readjusted to an average value of 2.1 SLPM (~ 230 W) for 8 minutes, at which point the reaction began to be exhausted.

The peak temperature was 58.7°C. During periods of high hydrogen production, the generator surface temperature climbed steeply. After an initial average temperature of 49°C had been established, the temperature began to track hydrogen production rate. Nominal flow rates of 2 SLPM (215 W) were accompanied by temperatures of 48-50°C.

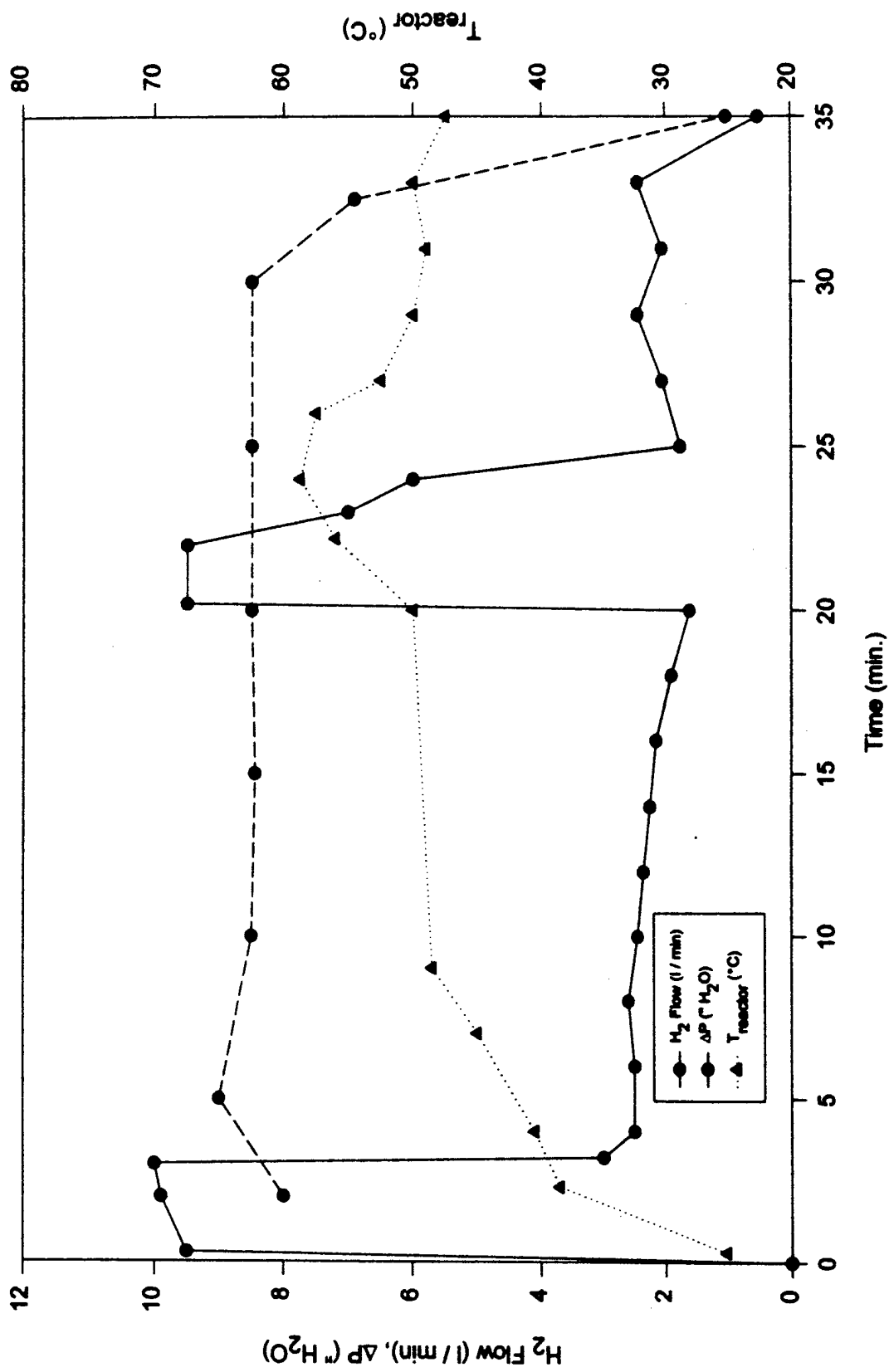


Figure 7. 2 blocks, 750 ml H₂O, T = 25°C

4. ESTIMATES OF TECHNICAL FEASIBILITY

The test results outlined in section 3 demonstrate that the generator is capable of producing hydrogen in sufficient quantity and with adequate purity for use in modern PEM fuel cells. Hydrogen flow can be controlled quite well. However, the generator must be maintained with the long axis within 45° of the vertical. Weight reduction and the elimination of attitude dependence relative to gravitational forces are the two main improvements to be addressed later. These future improvements, which affect the suitability of the unit for Army field use, are addressed in this section. The NaAlH_4 hydrogen source is also compared with a commercially available unit and with a concept developed and tested in Russia at the St. Petersburg Naval Academy.

4.1 Comparison to Existing Designs

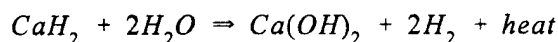
Hydrogen generators which utilize hydrolysis of hydrides have been tested in the laboratories of several companies and institutions. Different fuels have been used based on the preferences of the developers and the requirement for which the generator was developed. The two generators which the Phase I NaAlH_4 prototype is compared to are a unit developed by A. F. Sammer Corporation using calcium hydride (CaH_2) and a design developed in the St. Petersburg Naval Academy in Ptosk, Russia using sodium borohydride (NaBH_4). The CaH_2 unit is in commercial production. The Russian unit is a prototype which has features of both the Phase I unit and the CaH_2 unit.

The CaH_2 generator is a scalable unit potentially available in capacities up to several hundred watt-hours. A.F. Sammer markets this unit primarily for the support of medical devices which require 5-6 watts of power over several hours of operation. The calcium hydride fuel is supplied in the form of -30 mesh powder in a prefabricated canister. The canister contains absorbent material which utilizes wicking action to distribute reaction water evenly throughout the fuel cell. Water is fed to the generator via a stretched bladder whose volume is in excess of stoichiometric water requirements. As in the Phase I prototype, the pressure of product gas can be used to force water away from the hydride, and thus provide control of the reaction. Since CaOH (lime) is insoluble in water, the canisters are designed to be disposable. The generator is manufactured from titanium and aluminum, with a rubber water bladder. The fuel canister is manufactured from steel. The bladder is rechargeable via Luer fittings.

The generator developed at the St. Petersburg Naval Academy also uses pressure to force water contact with the hydride fuel source. Pressure is mechanically supplied by the operator through a rubber squeeze bulb which forces water from a reservoir to the hydride fuel container. The NaBH_4 fuel is supplied in the form of pressed tablets similar to that used in the Phase I prototype. Hydrogen product gas is stored in an accumulator for more consistent delivery of flow to a fuel cell. The reaction can be stopped by manipulation of valves which control product gas flow, access of the reaction water to the hydride fuel source, and venting of the water reservoir to

atmosphere to release accumulated pressure.

CaH₂ has a relatively low energy density compared to NaBH₄ and NaAlH₄. From the reaction



calcium hydride will produce 95 g of H₂ per kilogram of hydride. By comparison, the reactions for NaAlH₄ and NaBH₄ (see Table 1) produce 148 g H₂ and 212 g H₂ respectively per kilogram of hydride.

Calcium hydroxide (lime) is insoluble. The byproduct of the reaction of water with NaAlH₄ produces a soluble byproduct. The reaction byproducts are soluble to a concentration of 40-50% in water. The hydrate byproducts of the reaction of sodium boron hydride are soluble in excess water, as discovered by Bloomfield, et.al. Work done in Russia indicates solubility to 33% in excess water. Solubility of sodium boron hydride byproducts can be increased by increasing the temperatures at which hydrolysis takes place (Efimov, 1997). As mentioned previously, NaBH₄ requires catalytic action from Co, Fe, or other metals to control pH in the reaction liquid. The complete solubility of byproducts may vary with choice of catalysts and binder materials.

The amount of heat produced per mole of hydrogen is roughly the same for each of these hydrides. As can be seen from Table 2, CaH₂ and NaAlH₄ produce approximately 111 kJ per mole of hydrogen. Calculations done at the St. Petersburg Naval Academy indicate approximately 117 kJ of heat per mole of H₂ produced from the reaction. The CaH₂ unit reaches external temperatures of 50-60°C over a period of 6 hours. The internal temperatures of the reaction of sodium boron hydride are comparable to NaAlH₄ (90-95°C), but no figures are given for the external temperature of the generator.

Both NaBH₄ and NaAlH₄ were found to be readily available in Russia. CaH₂ is commercially available in the United States. Estimated retail costs of CaH₂ based on cartridges supplied by Sammer Corporation for their product line is \$87/kg CaH₂. Since this cost includes the manufacture of the cartridge and the packaging of the hydride, the actual cost of CaH₂ is less in dollars per kilogram. Bloomfield, et.al., cite the low cost of NaBH₄. However, since NaBH₄ requires catalytic additives as well as binders, the final cost of this fuel is dependent upon the selection of a combination of ingredients that minimizes cost as well as providing suitable reaction characteristics. The current cost of the pressed tablets of NaAlH₄ is \$200/kg. This cost is based on the current low-volume, relatively expensive manufacturing technique described in section 2. The proprietary technique mentioned developed at the State Scientific Center of the Russian Federation in Moscow would contribute to a reduction in costs of the pressed hydride.

Given the prototypical nature of the Phase I unit and the St. Petersburg Naval Academy concept, it is difficult to compare system weights for purposes of suitability. Both the Phase I and Naval Academy prototypes could be redesigned to reduce system weight while retaining essential

functionality. Also, each unit is designed with different production rates in mind. The CaH_2 medical support unit runs at flow rates of between 0.010 and 0.150 ℓ/min . The Phase I prototype unit and the St. Petersburg Naval Academy unit can run at rates as high as 10 SLPM. The capacity of the St. Petersburg unit is also greater, utilizing 600 g of NaBH_4 , whereas the Phase I prototype utilizes between 35 and 140 grams (1-4 pellets). Based on reaction stoichiometry, the (50 liter H_2) Sammer unit uses 58.5 g of CaH_2 . However, it is possible to make some comparisons based on scaling unit production of the generators to a standard. Table 3 is a comparison of the various parameters associated with these units. The weights shown in this table represent the equivalent weights compared to the 50 ℓ CaH_2 unit.

As can be seen from the table, the Phase I prototype is comparable to the commercial unit in volume of H_2 production per kilogram of system weight. Further development will decrease the total weight and increase the volume of H_2 production per kilogram of system weight. This goal will be strongly aided by the low pressure reaction. The adoption of new techniques for the production of sodium aluminum hydride should lower the fuel cost to a value more competitive with other hydrides. In safety and ease of handling, the generator design is competitive with commercial products such as the CaH_2 generator.

4.2 MII/RTI Generator Design and Future Work

The generator described in this report was built from copper. Copper has excellent heat transfer properties, was resistant to the alkaline byproduct of the reaction, and was easily formed for prototype development. A finished product utilizing this same design would need to be lighter, have as good as or better heat transfer properties, be tolerant of the rough handling of field use, and would ideally be attitude (position) independent for normal operation.

The generator could be mass-produced using molded plastic. Several different plastics, including glass-filled epoxy, high-impact ABS, CTFE (a fluoropolymer), phenylene oxide plastics, and polysulfone plastics have the necessary resistance to alkaline materials and can tolerate the heat of the reaction. An alternative is stainless steel. While heavier than plastic, stainless steel is lighter than copper. Because the pressures of the reaction are low, generator design does not have to emphasize strength for containment. This will contribute to minimum weight in a finished product.

The fins used for cooling in the prototype would be redesigned for a field unit. In their current form, they add to the volume of the unit, which decreases portability and ease of handling. Their function could be handled in different ways. Since convective cooling is necessary, the generator outer cylinder could have molded or machined airways which facilitate convection. This construction could also serve as a heat shield between the user and the generator surface. Since the byproduct is soluble and does not adhere to the interior surface, this would not complicate cleaning of the generator, and reduces effective volume by 45%.

Table 3: Comparison of Parameters

	Magnic International/Research Triangle Institute Phase I Prototype	CaH ₂ (A.F. Sammer 50 l unit)	St. Petersburg Naval Academy Prototype
Unit Internal Pressure (Maximum psi)	0.36	30.0	Not Available
Controllable Reaction	Yes	Yes	Yes
Fuel Source	NaAlH ₄	CaH ₂	NaBH ₄
Energy Density (g H ₂ / kg Hydride)	148	95	212
H ₂ Production (Maximum SLPM)	10	0.150	Not Available
Soluble Byproduct	Yes ¹	No	Yes ²
Generator External Temperature (Maximum °C)	58.7	60	Not Available
Fuel Cost (US \$/kg)	200	87 ³	Not Available
Unit Cost (US \$)	N/A	500	N/A
Unit Weight (kg)			
Generator	0.50	0.60	< 0.3 ⁴
Fuel + Water	0.18	0.20	< 0.15 ⁴
Ancillary Equipment	0.15	0.15	Not Available
Total	0.83	0.95	< 0.7 ⁴

¹ Soluble to 50% in excess water

² Solubility dependent on fuel constituents

³ Includes cost of cartridge

⁴ Unit is a bench-scale prototype

The final unit will retain the outer shell, the inner shell, and the hydride pellet support. The threaded fitting which is used to attach the inner and outer cylinders would be replaced with a single-twist locking device which would facilitate ease of use, speed recharging, and prevent potential cross-threading of the joint. Alternatively, small over-center clamps could be used with a hinged lid. Because the unit operates at atmospheric pressure in the outer cylinder and because the hydrogen is sealed from the joint of the inner and outer cylinders, no positive sealing is needed at this joint, which simplifies construction.

It is planned that attitude insensitivity be included in the next design. This is planned to be accomplished by incorporating a robust, simple, spring-loaded plunger design integrated into the water containing outer shell of the Phase I generator design. This approach is an alternative to the bladder pressure approach incorporated in the commercial design described earlier. The spring for this design will be manually set and is designed to produce nearly-constant tension to allow approximately 0.07 atmosphere (1 psig) on the water entering the fuel chamber, rather than a steadily decreasing pressure which begins at a high value (e.g., 1-2 atm). Since typical generator dimensions will not require a water chamber in excess of 50 centimeters in length, a pressure of 0.07 atm should be more than sufficient, even if the generator is inverted. Some attention must, of course, be given to vapor pressure and hydrogen solubility in the water, although these factors are a small contributor in maintaining the gas/water pressure balance.

An alternate scheme which the research team has considered is to mount the generator in a shell with gimbaled bearings at the points of contact. The generator could be constructed to orient itself in an upright position with respect to horizontal at any angle relative to the vertical. Disassembly for charging and cleaning could be accomplished with appropriate shell design. If the shell is vented to atmosphere and the generator remains upright, the low-pressure reaction can be preserved without the need for forcing water under high pressure into contact with the hydride. Proper shell construction can also aid in cooling.

The control valve will be integrated into the hydrogen source package. The valve control may be instituted as a push button-type device, or another simple mechanism which provides on/off control. Hydrogen demand will be controlled by electrical power requirements, and associated fuel cell demand. Therefore valve control will only require opening and closing. The fuel source package will be integrated with the fuel cell. The research and development team will select the best commercially available, or more likely, best prototype candidate for light weight, high reliability manufacture. Discussions have been held with a number of fuel cell developers and manufacturers to obtain dimensions, performance, characteristics and prices. The research team sees no extensible obstacles that would prevent the final design and fabrication of this totally integrated fuel source and power output electrical power pack. The options for optimizing performance and packaging of a PEM fuel cell in the required power range are not yet well defined. However, it is believed that collaboration with fuel cell manufacturers will make these options clear and that optimization can be reached. The design challenges can be met to improve the prototype and offer a cost effective, reliable, manufacturable product. The attitude insensitive operation and materials modifications are underway.

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