High Density Hydrogen Storage System Demonstration Using NaAlH_4 Based Complex Compound Hydrides

Final Report

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Executive Summary

1 Executive Summary

From 2001 to 2007, the United Technologies Research Center (UTRC), in collaboration with the organizations acknowledged above, performed research to design, fabricate and test prototype hydrogen storage systems based on the complex hydride NaAlH_4 . This material was selected because of its recent discovery of being reversible with the addition of titanium and because it possessed the highest gravimetric capacity of any material having acceptable charging pressures and discharging temperatures. If a superior material had been discovered during concurrent research by the hydrogen storage community, it would have been incorporated into the system development, but NaAlH_4 remained the best material throughout the duration of the contract.

Consistent with the Statement of Project Objectives in Section 2.2, the approach taken was to construct two prototypes, with each effort having aspects which focused on the hydride material and others which addressed the system / component technologies. The original plan was to develop the two prototypes based primarily on existing conventional metal hydride systems and having hydrogen capacities of 1 kg and 5 kg. The first system scale was as originally planned. However, significant additional challenges were associated with the NaAlH_4 based system such as the use of a composite vessel, additional reactivity issues, greater requirements for purity during fabrication and more difficult powder loading. As a result, the second prototype was fabricated at the 1/8 kg H_2 scale in order to facilitate the pursuit of more advanced design and fabrication concepts.

As part of the material studies for Prototype 1, reactivity tests were conducted with water and air in a number of standardized configurations, which gave a semi-quantitative measure of the material behavior. One conclusion from this materials testing was to exclude the use water as a heat transfer liquid in the system design. A figure of merit, termed the *convective efficiency*, was derived and used to select a high performance, inert oil, ParaTherm MR. The tests also influenced the selection of fabrication and testing configurations, hardware and procedures.

Other materials testing throughout the project examined the use of alternate catalysts (dopants) and processing methods. The use of scandium and oxides was found to perform well for low temperature and low pressure absorption, but not for low temperature desorption. Due to the rapidly increased cost of TiCl_3 , TiF_3 was used to produce the > 25 kg of material synthesized for Prototype 1. While TiF_3 was found to work adequately for small scale, high energy ball milling, it did not perform as well with large scale milling. In subsequent efforts for Prototype 2, scaled-up attrition milling with the low cost $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ catalyst was found to work well. Though the attrition mill became unavailable and synthesis of the Prototype 2 material was performed using small batch SPEX milling, the use of slurry attrition milling, nevertheless, was found to offer a viable route to scale up mechanical milling for large scale production of such hydrogen storage materials.

Materials tests were conducted to examine the cyclic degradation of storage capacity. Using standard purity hydrogen (99.95%), the capacity drop was found to depend on the catalyst type and was at least 10% over 20 cycles. Powder densification tests using a number of different approaches were conducted, indicating that the fine-scale, non-conductive particles were a challenge to pack. Materials tests were also performed to determine the reaction kinetics for a wide range of temperatures and pressures. This data was then used to determine parameters for a novel kinetics model which tracked the two-step desorption/absorption reactions of NaAlH_4 . The kinetics model was then implemented into the finite element code ABAQUS for heat exchanger optimization.

Executive Summary

Due to the moderately high pressures required to recharge NaAlH_4 compared with conventional metal hydrides (ex. LaNi_5), a carbon fiber composite vessel was employed. Beyond applicability to NaAlH_4 , having high pressure capability for the system increases its potential for use with other, to-be-discovered reversible hydrides. Due to the high reactivity of the hydride and the high resin curing temperatures of the composite, it was considered infeasible to wind the composite overwrap after filling the thin vessel liner with hydride. Therefore, the powder had to be loaded after the composite material was cured. Prototype 1 used a fine-scaled open-cell aluminum foam to enhance heat transfer. Because of the risk in filling the aluminum foam with hydride using conventional means of simply pouring (the powder can clump and clog, preventing further loading), the composite vessel for Prototype 1 was made with a fully open end, recognizing this would add significant weight. As described in Section 4.5.3, this allowed the heat exchanger aluminum foam disks to be loaded with powder prior to insertion into the composite vessel. With this experience gained, one of the focal points for Prototype 2 was to develop a powder loading procedure and compatible heat exchanger design which would permit the fabricated vessel / heat exchanger to be loaded to high densities through a small (1/2" diameter) port. This effort was successful, with the average hydride density increasing from 0.44 g/cc for Prototype 1 to 0.72 g/cc for Prototype 2 and the pressure vessel weight decreasing substantially.

Simulation development for heat exchanger design and optimization was supported by a number of experiments measuring hydride thermal conductivity, thermal contact resistances and conduction enhancement performance. Along with the kinetics model mentioned above, these results were incorporated into the development of a transient thermo-chemical finite element simulation tool using the commercial code ABAQUS. Simulations were conducted for a variety of steady state and transient conditions which were applied, in conjunction with unique modeling and optimization methods, to develop the best heat exchanger designs given certain constraints due primarily to fabrication limitations. A general phenomenon to note is that a material with rapid reaction kinetics over a wider temperature range can tolerate a larger temperature differential and therefore can perform with a lower mass heat exchanger. Another result from the studies is that the heat exchanger mass is reasonable for refueling times in the neighborhood of 15 to 20 minutes. Roughly speaking, to halve the refueling time, the heat exchanger mass needs to be doubled. Thus, achieving a 10 minute refueling time will have a moderate weight penalty, but is still reasonable (for reversible materials having reaction enthalpies between 30 and 40 kJ / mole H_2 and typical temperature range widths comparable to NaAlH_4). Heat removal for a 3 to 5 minute refueling time will be increasingly challenging using the current class of material and heat exchange technology.

The heat exchanger for Prototype 1 used 4% dense aluminum foam as the conduction enhancement between the tubing which carries the heat transfer liquid. As discussed in Section 6.2.1, low density conductive foams have some advantages but also have a significant disadvantage that only approximately 1/3 of the material is participating in the long range heat transport from the tubing. For this reason and for improved powder loading, finely spaced fins were used in Prototype 2. Simulation was very beneficial to optimize the tubing diameter, tubing spacing, fin thickness and fin spacing. This resulted in an estimated 30% reduction in heat exchanger mass compared with Prototype 1. Combined with the increase in powder density and reduction in pressure vessel mass, the as-fabricated performance improved significantly (Table 2).

Executive Summary

A summary of the performance metrics for the as-fabricated and projected prototypes is given in Figure 1. A number of the projection elements are detailed in Section 7.1. Others have been made on a high level, i.e. without specific methods as to *how* these would be achieved, but with a goal to balance the challenges for the material versus the system. From this, to meet the DOE 2007 target, a 6.5 wt% material would be needed with a packed powder density of 0.8 g/cc and system gravimetric efficiency of 0.67 when also including the hydrogen stored as compressed gas within the powder void volume. The 2010 target requires an 8.0 wt% material, 0.850 g/cc packing and system gravimetric efficiency of 0.75.

Complex Compound Hydride Storage System (CCHSS) Performance Metrics

Material & Version:		NaAlH ₄ Prototype 2	NaAlH ₄ Projected	TBD hydride	TBD hydride	DOE Targets	
Characteristics & Metrics	Units					2007	2010
Material gravimetric capacity	% kg H ₂ / kg hydride	3.4%	3.4%	6.5%	8.0%		
H ₂ charging pressure	bar	100	100	70	50		
Packed powder density	kg hydride / m ³ powder	720	850	800	850		
Material volumetric capacity	kg H ₂ / m ³ powder	24	29	52	68		
System gravimetric efficiency	kg hydride / kg system	0.515	0.63	0.67	0.75		
System volumetric efficiency	m ³ powder / m ³ system	0.76	0.76	0.7	0.7		
Normalized compressed gas	% kg H ₂ gas / kg hydride	0.5%	0.3%	0.3%	0.2%		
System gravimetric capacity	% kg H ₂ / kg system	2.0%	2.3%	4.5%	6.1%	4.5%	6.0%
System gravimetric capacity	kWh / kg	0.66	0.8	1.5	2.0	1.5	2.0
System volumetric capacity	kg H ₂ /m ³	21.1	24.0	37.8	48.6	36	45
System volumetric capacity	kWh / L	0.70	0.80	1.26	1.62	1.2	1.5

Notes

a: Improved catalysts & processing

b: Demonstrated powder packing enhancement

c: Improved densification & size scaling

d: Materials discovery

e: Reduction of charging pressure & vessel mass

Figure 1: System performance metrics status and projections.

Future development areas which can contribute to performance improvements include:

- Greater powder densification along with engineered hydrogen mass distribution that are compatible with overall system fabrication procedures.
- Continued heat exchanger enhancement such as size scale reduction for fluid flow channels which also is sufficiently lightweight and application of higher performance yet chemically inert heat transfer liquids.
- Vessel liners which are lighter-weight than stainless steel and can withstand elevated temperatures as well as hydride chemical exposure.

Overview

2 Overview

This final report describes the motivations, activities and results of the hydrogen storage independent project *High Density Hydrogen Storage System Demonstration Using NaAlH₄ Based Complex Compound Hydrides* performed by the United Technologies Research Center (UTRC) under the Department of Energy (DOE) Hydrogen Program, contract # DE-FC36-02AL67610. This effort officially began in April of 2002 and performed technical research through March of 2007 with subsequent concluding activities and reporting. DOE financial support totaled \$2,715k with UTRC contributing \$1,066k (28.2%) of cost share resources.

2.1 Project Motivations and Scope

It is well recognized that storage of hydrogen in a compact and lightweight form is critical to the commercial introduction of hydrogen as an energy carrier, particularly for automotive fuel cells, with the benefits of reduced dependence on foreign oil and increased potential for utilizing renewable energy sources. According to the National Academies' February 2004 report on the DOE Hydrogen Program:

"A transition to hydrogen as a major fuel in the next 50 years could fundamentally transform the U.S. energy system, creating opportunities to increase energy security through the use of a variety of domestic energy resources for hydrogen production while reducing environmental impacts, including atmospheric CO₂ emissions and criteria pollutants."

The major classes of established hydrogen storage methods are compressed gas, cryogenic liquid, metal hydrides, chemical hydrides and adsorbents, all of which have advantages and disadvantages, but none is clearly superior for automotive transportation. High pressure compressed gas systems have been certified for automotive use, but do not meet all of the desired targets. Cryogenic liquefied hydrogen has a substantial energy penalty of over 30% for production and is susceptible to boil-off issues. A disadvantage of conventional metal hydrides is their low hydrogen capacities of less than 2 wt% for alloys with discharge temperatures where the waste heat of a PEM fuel cell (~ 90°C) can be used to release the hydrogen. Chemical hydrides, while potentially having high capacities, must be regenerated off-board of the vehicle and can require a substantial amount of energy to reprocess.

Complex hydride materials have the potential to store higher capacities of hydrogen than conventional metal hydrides for indefinite periods of time and require only moderate hydrogen gas pressures for recharging. Associated with this are lower energy losses compared with high pressure gas compression and liquefying processes. Challenges include minimization of system components' weight & volume, removal of heat during recharging and cyclic durability. Many of these critical barriers to achieving commercially viable solid state hydrogen storage devices have been identified in general, but only through experience, such as in this effort, can the significance of the detailed systems requirements be fully appreciated.

The objectives of the program were to identify and address the key systems technologies associated with applying complex hydride materials, particularly ones which differ from those for conventional metal hydride based storage. This involved the design, fabrication and testing of two prototype systems based on the hydrogen storage material, NaAlH₄, which had recently (at the time of the project proposal) demonstrated surprising reversible capacity with the addition of titanium (Ref. 1).

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Goals for the prototype were driven by the emerging and revised DOE technical targets for hydrogen storage given in Table 1. Because the storage capacity of NaAlH_4 (5.56 wt% theoretical; nominally 4 wt% in practice) is not high enough to meet the system gravimetric capacity target, the intention was to consider other higher capacity complex hydrides for later stages of the project as they were discovered. However, no such materials were developed / reported by the world-wide research community with better characteristics and viability for on-board recharging than NaAlH_4 . Therefore, development of the systems technologies were focused on NaAlH_4 , but have applicability to other Complex Compound Hydride (CCH) materials with similar thermodynamic characteristics.

Table 1: DOE technical targets for on-board hydrogen storage systems.

Storage Parameter	Units	2007 Target
System Gravimetric Capacity	kg H_2 / kg system	0.045
System Volumetric Capacity	kg H_2 / L system	0.036
System Fill Time ¹	min	10
Minimum Full Flow Rate	(g/s) / kW	0.02
Storage System Cost	\$ / kg H_2	200
Cycle Life	Cycles	500
Safety	N/A	Meets C&S

¹ For a 5 kg H_2 refueling quantity.

The storage system which contains the CCH powder must serve two primary functions: (1) exchange heat between the powder and a working liquid to drive the absorption/desorption of hydrogen; (2) support elevated hydrogen pressure during refueling. These functions must be performed with a minimum of weight, volume and cost. In addition, there are other secondary characteristics such as (i) allow for significant volumetric change of the powder, (ii) exchange of hydrogen without the loss of the fine CCH powder particles, (iii) maintain chemical compatibility with the CCH powder and with hydrogen, (iv) produce minimal impurities going to the fuel cell (PEM FC) and (v) fit into a conformable volume.

Prior designs for conventional metal hydride systems, such as those by Savannah River National Laboratory, contain many elements that are common to other designs such as a cylindrical pressure vessel, metal foam heat conduction enhancement, internal conduit for the heat transfer liquid, partitions and a particle filter. These and other concepts are the result of a substantial amount of activity which took place approximately 20 to 30 years ago in hydride bed system design for use with conventional metal hydrides. Many metal hydride materials have very fast reaction kinetics so that the transfer rate of hydrogen is limited by the transfer rate of heat. In contrast, the current NaAlH_4 material is limited by the reaction kinetics when incorporated into a heat exchanger having only moderate heat transfer capability.

Initially, the system design was anticipated to more closely resemble that of conventional metal hydride systems, with the emphasis being to develop 1 kg and 5 kg H_2 full scale prototypes. As knowledge was gained about system integration of the relatively novel NaAlH_4 , significant design and fabrication changes were pursued including the use of high temperature composite pressure vessels and solutions to powder loading and densification challenges. The first prototype was designed and constructed at the 1 kg H_2 scale (19 kg of NaAlH_4) and had a fully opened end in the composite vessel to provide adequate means for loading the hydride powder within the metal foam heat exchanger. The second prototype was produced at $(1/2)^3 = 1/8^{\text{th}}$ scale of Prototype 1 to be able

Overview

to apply more complex fabrication methods while keeping investment in supporting assembly hardware to a reasonable level. This enabled the development of a lighter weight composite pressure vessel and finned tube heat exchange along with more effective powder loading methods to achieve substantial improvements, particularly for the as-fabricated gravimetrics and volumetrics given in Table 2.

Table 2: Summary of Prototype Gravimetric and Volumetric Performance.

		As-Fabricated		Projected	
Metric	Units	Prototype 1	Prototype 2	Prototype 1	Prototype 2
Gravimetric efficiency	kg hyd. / kg sys.	0.14	0.515	0.48	0.60 – 0.63
Gravimetric density	% kg H ₂ / kg sys.	0.4%	2.0%	1.7%	2.3%
Powder density	g / cc	0.44	0.72	0.60	0.85
Volumetric density	Wh / L	200	700	600	800

The structure of the report is divided into primary sections which follow the Statement of Project Objectives given below. Descriptions for many of the abbreviations can be found in Section 10. More detailed derivations and descriptions have been placed in the appendices. This document was prepared in Microsoft Word, and if an electronic copy is available, the Document Map feature can be used to facilitate navigation from section to section.

2.2 Statement of Project Objectives

An abbreviated and updated version of the Statement of Project Objectives is given below which also serves as an outline to the report.

Prototype 1

• Media Studies

- Conduct standardized safety testing related to the classification of hazardous materials for catalyzed NaAlH₄.
- Create combined atomistic/thermodynamic models of the NaAlH₄ system.
- Experimentally characterize various media/catalyst compositions.
- Cyclically evaluate selected catalyst compositions to determine degradation.

• System Studies

- Develop preliminary designs through the evaluation of existing systems, generation of weight/volume improvements, and high level optimization.
- Perform heat and mass flow modeling for detailed optimization.
- Conduct preliminary system performance modeling analyses of the combined PEM FC / H₂ Storage system.
- Design and fabricate a one end closed composite tank capable of 100 bar sustained pressurization at 250°C sized to contain sufficient hydride for a nominal 1 kg H₂ capacity.
- Develop synthesis methods for fabricating media in the quantities required for the first prototype.
- Develop media packing methods consistent with the prototype designs.
- Develop fabrication facilities and methods for safe assembly of the first prototype.

Overview

- Construct an evaluation facility to safely and accurately measure system performance.
- Evaluate the performance of the first prototype system for static charging and discharging rates.
- Establish the performance metrics of the first prototype in-situ rechargeable solid hydrogen storage system.
- Develop and demonstrate a neutralization procedure for the NaAlH_4 system.

Prototype 2

• Media Studies

- Experimentally characterize various media/catalyst compositions.
- Assess the effects of air and humidity exposure on composition in catalyzed NaAlH_4 using time resolved XRD.

• System Studies

- Develop second generation preliminary designs.
- Perform heat and mass flow modeling for detailed optimization.
- Design a compact heat exchange fluid manifold.
- Fabricate a second generation heat exchange system.
- Develop new synthesis methods for fabricating media in the quantities required for the second prototype design.
- Develop media packing methods to achieve packing densities consistent with gravimetric and volumetric requirements.
- Design and fabricate a new composite vessel including an integral domed liner / oil manifold optimized to minimize weight.
- Fabricate a prototype H_2 storage system of nominally 50 g H_2 scale.
- Evaluate the performance of the second prototype for static charging and discharging rates.
- Assess modeled system performance with actual performance.
- Deliver a list of all component weights and volumes for the prototype system.
- Deliver requirements for both material and system based on knowledge gained to meet 2.5 wt% and 4.5 wt% system metrics.
- Perform preliminary experiments and analyses to evaluate candidate new materials for system application and projected performance.

Prototype 1 Media Studies

3 Prototype 1 Media Studies

In this section, the elements of evaluating and developing the NaAlH_4 hydride material for the first prototype will be described as outlined in Section 2.2.

3.1 Safety Testing and Analysis

3.1.1 Testing Overview

Safety issues related to accidental damage of NaAlH_4 systems as well as laboratory research are a concern and little information is available in the open literature. Safety studies examining how this material will react upon sudden exposure to heat, moist air and water have been examined by Frank Lynch of the subcontractor HCL. These tests have been based on the UN document “Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria” (Ref. 2) that serves as the basis for US DOT HAZMAT shipping classifications. The material classifications and associated tests are as follows:

- Division 4.1: flammable solids
 - Burn rate
- Division 4.2: spontaneous combustion
 - Pyrophoric solid
 - Self heating
- Division 4.3: dangerous with water
 - Immersion
 - Surface exposure
 - Droplet

The standard test devices were constructed for these tests.

Dust explosion testing was conducted by Kidde-Fenwal, Combustion Research Center in which the following characteristics were measured by the associated ASTM tests:

- P_{max} & $(dP/Dt)_{max}$ (ASTM 1226)
- Minimum Explosive Concentration (ASTM 1515)
- Minimum Ignition Energy (ASTM 2019)
- Minimum Ignition Temperature (ASTM 1491)

While this collection of tests is not specific to automotive fuel tanks, following these established procedures puts catalyzed NaAlH_4 into perspective with a large database of other flammable, self-heating, water reactive and dust explosive materials.

The material evaluated was composed of commercial grade NaAlH_4 combined with 2 mol% TiCl_3 catalyst and was tested in three states, produced by the following procedures. All material was ball milled for 24 hours, exposed to the pressures and temperatures below and shipped in approved, pressure rated sample bottles at 100 psi of nitrogen.

- State A - Fully Charged (NaAlH_4): 2.5 ksi H_2 / 100°C / 8 hrs.
- State B - Partially Discharged ($\text{Na}_3\text{AlH}_6 + 2\text{Al}$): 0.6 ksi H_2 / 150°C / 8 hrs.
- State C - Fully Discharged ($\text{NaH} + \text{Al}$): vacuum / 240°C / 8 hrs.

Prototype 1 Media Studies

3.1.2 Burn Rate Testing

As its name implies, the Burn Rate Test measures the propagation speed of a flame front for an elongated pile of powder having specific geometry.

The steps in the method are

1. Material is packed into a 250 mm trough in a H_2 atmosphere & pressurized to 1000 psi.
2. The trough is dropped three times from a height of 20 mm to settle to a standard state.
3. It is then quickly removed to air, inverted, raised leaving the powder pile and ignited at one end in 3 to 5 seconds after initial removal.
4. Measurement of the flame propagation is obtained through video and the time to travel from 80 mm to 180 mm is recorded.

Figure 2 shows a powder train of surrogate material produced by the standardized sizing and settling procedures.

Figure 2: Configuration of UN/DOT burn rate test.

Behavior during a representative burn rate test on the fully discharged material, $NaH+Al$, is shown in Figure 3. Results from testing on all three compositions are given in Table 3 for both an ambient starting temperature of nominally $20^{\circ}C$ and at the elevated temperature of $80^{\circ}C$ that would represent the powder condition within a storage system heated during hydrogen discharge. The results are significantly greater than the 2.2 mm/s threshold to classify the material as Division 4.1.

Prototype 1 Media Studies

Figure 3: Burn rate testing of the fully discharged composition, NaH+Al.

3.1.3 Pyrophoricity Testing

The procedure to test for pyrophoricity is as follows:

- Material quantity: 1 to 2 ml of powder (at ambient temperature of $\approx 20^{\circ}\text{C}$)
- Pour the material from a height of 1 meter onto a non-combustible surface
- If the substance ignites during the drop or in the subsequent 5 minutes, it is pyrophoric and the material is classified as Packing Group I or the highest risk category.
- Repeat 6 times unless there is a positive result during one of the prior trials

Results from the pyrophoricity testing are given in Table 3, listed as Spontaneous Ignitions. Note that for the current material and processing, the material is not pyrophoric according to shipping test standards (20°C), but if we preheat the material to a temperature at which a system might operate (80°C), then the partially discharged material is pyrophoric. This is an example of how standardized tests can serve as a starting point, but there may be sound reasons to adapt them to evaluate better the material behavior under more relevant conditions.

Prototype 1 Media Studies

3.1.4 Self Heating Testing

The objective of the Self Heating Test is to determine if material spontaneously self heats or ignites upon exposure to air. In the procedure,

1. The material is packed into a stainless steel basket having 0.05 mm mesh openings.
2. A thermocouple is inserted into center of sample.
3. The first basket is inserted into a secondary stainless steel mesh containment and secured.
4. The assembly is placed in a convective air furnace at 140°C and the internal specimen temperature is monitored. Testing with starting temperatures of 100°C and 120°C was also conducted.
5. A positive test for the Division 4.2 material classification occurs if the sample temperature is more than 60°C above the oven temperature at any time during the 24 hour test.
6. Testing can be conducted in either order with the 100 mm³ and 25 mm³ baskets – see Figure 4. The material will be classified Packing Group II if the 25 mm³ test is positive and Packing Group III if the 100 mm³ is positive and the 25 mm³ test is negative (along with other specifications).

Figure 4: Experimental configurations for standardized self heating tests. The 25 mm³ sample was used in the testing due to the anticipated positive test results.

Representative temperature data for a test is plotted in Figure 5 in which the temperature increase of >60°C is far surpassed to the point that the type K thermocouple was destroyed. Results for the three compositions using the 25 mm³ basket are given in Table 3. The fully hydrided and partially hydrided states exhibit dangerous self heating at the lowest starting temperature of 100°C while the fully discharged material does not until a starting temperature of 140°C, all three being Packing Group II materials.

Prototype 1 Media Studies

Figure 5: Results for self heating test on Na₃AlH₆ material preheated to 100°C indicating Dangerous Self Heating.

3.1.5 Water Reactivity Testing

Water reactivity is measured in a number of configurations. In one, a small quantity of powder is dropped into a greater quantity of water as shown in Figure 6 for State B (Na₃AlH₆). An alternate configuration is shown in Figure 7 having a smaller quantity of water than hydride.

Results from these tests and others are given in Table 3. The conclusion drawn regarding the purpose of these UN/DOT materials transportation tests is that the material changes classification from a CFR 49 Division 4.3, Packing Group II material to Packing Group I, which has implications on how it must be packaged, what quantities that can be shipped and the vehicles that can be used.

Figure 6: Water immersion test for partially discharged Na₃AlH₆.

Prototype 1 Media Studies

Figure 7: Water drop test for partially discharged Na_3AlH_6 .

Table 3: Results of the UN/DOT safety tests.

Test Method	Ref. UN33.	State A (NaAlH_4)	State B (Na_3AlH_6)	State C (NaH)
Prelim. Screening	2.1.3	Yes, Flammable Solid	Yes, Flammable Solid	Yes, Flammable Solid
Burning Rate	2.1.4	51 mm/sec	222 mm/sec	27 mm/sec
Burning Rate, 80C	Note 1	127 mm/sec	spontaneous ignition	40 mm/sec
Spontaneous Ignition, R.T.	3.1.4	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric
Spontaneous Ignition, 80C	Note 1	6 Tries, No Ignition	1 Try, Ignited	6 Tries, No Ignition
Dangerous Self-Heat, 100C	3.1.6	Yes, Dangerous	Yes, Dangerous	Not Dangerous
Dangerous Self-Heat, 120C	3.1.6	Not Tested (Note 2)	Not Tested (Note 2)	Not Dangerous
Dangerous Self-Heat, 140C	3.1.6	Not Tested (Note 2)	Not Tested (Note 2)	Yes, Dangerous
Dangerous When Wet	4.1	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1

Note 1: This is not a UN standard test. We want to know what happens when this material is spilled at operating temperature of 80C. All other details are per UN burn rate and spontaneous ignition test specifications.

Note 2: This test was not necessary, since this material had already shown dangerous self-heating at 100C.

3.1.6 Dust Explosion Testing

In portions of this testing, a standard 20 liter testing apparatus, shown in Figure 8, is used in which the chamber is partially evacuated and then the powder is injected into the chamber via the rapid flow of air and the use of specially designed nozzles to obtain a finely dispersed dust cloud with uniform concentration.

Prototype 1 Media Studies

Figure 8: Standard 20 liter dust explosion apparatus.

Results from the suite of tests listed in Section 3.1.1 are given in Table 4 for State A (fully charged) and State C (fully discharged) materials as well as for two commonly used reference materials. The State B material (partially discharged) was felt to be too reactive, based on the data of Table 3, to test using the standard procedures and equipment. The two tested states have the highest dust classification of “St-3” or “Highly explosive” when finely divided. The Minimum Ignition Energy (MIE) is below the threshold detectable by the system. A level of less than 10 mJ indicates that static electricity sparks would have enough energy to be a concern for ignition.

Table 4: Results from dust explosion tests on fully charged and full discharged materials.

	Test Materials		Reference Materials	
	NaAlH ₄	NaH+Al	Pitt. Seam Coal Dust	Lycopodium Spores
P _{max} bar-g	11.9	8.9	7.3	7.4
R _{max} bar/s	3202	1200	426	511
K _{st} bar-m/s	869	326	124	139
Dust Class	St-3	St-3	St-1	St-1
MEC g/m ³	140	90	65	30
MIE mJ	<7	<7	110	17
T _c °C	137.5	137.5	584	430

Prototype 1 Media Studies

3.2 Atomistic and Thermodynamic Modeling

Initial development and application of combined atomistic and thermodynamic modeling was conducted under the present contract to assess its potential in predicting: (i) phase diagrams and (ii) thermal stability of catalyzed compounds. The techniques developed were matured further in a separate DOE Hydrogen Storage contract, DE-FC36-04GO14012, focused on the discovery of novel storage compounds. With this method, the structure and thermodynamics of NaAlH_4 in its hydrided and dehydrided forms were evaluated using the ab initio code, VASP, and thermodynamics code, ThermoCalc in partnership with QuesTek Innovations. Atomistic calculations were used to determine stable ground state structures as shown in Figure 9 and to predict ΔH_f at 0K.

Figure 9: Ground state structures of NaAlH_4 and dehydrided products.

Thermodynamic calculations determined ΔG_f versus temperature and pressure which were then used to construct phase diagrams. Predicted phase diagrams for the Na-Al-H ternary system are shown in Figure 10. Comparisons with experiment are given in Figure 11. The agreement for the data shown here as well as for other comparisons was reasonably good, giving confidence that the modeling can be predictive and support development of new or modified storage materials. Predicted phase diagrams for the Na-Al-Ti-H system are given in Figure 12. Further development and application of these methods were pursued in the above referenced contract.

Prototype 1 Media Studies

Figure 10: Predicted phase diagrams for Na-Al-H system.

Figure 11: Preliminary comparison of predicted phase diagrams with experiment.

Figure 12: Na-Al-Ti-H phase diagrams; (a) 100°C & 1 atm H_2 ; (b) 100°C & 100 atm H_2 .

Prototype 1 Media Studies

3.3 Chemical Reaction Development

3.3.1 Catalyst Experiments

In the pursuit of improved reaction kinetics and capacity, a variety of catalyst compositions were evaluated during the development effort for the first prototype. Commercial grade NaAlH_4 was purchased from the Albemarle Corporation with a chemical certification analysis of 86.3% NaAlH_4 , 4.7% Na_3AlH_6 , 7.5% free Al and 10.1% insoluble Al (with all analyses given in wt%). The NaAlH_4 was mixed with additions of 6% TiCl_3 , 4% TiCl_3 , 3.3% ScCl_3 +2% Na_2O , 4% CeCl_3 and 6% TiF_3 using high energy SPEX ball milling for three hours under nitrogen. Immediately after ball milling, approximately 1 g of the sample was transferred into the sample holder of a modified Sievert's apparatus from Advanced Materials Corporation. The storage and transferring of the materials were performed under a high purity nitrogen environment inside of a glove box with an oxygen concentration <10 ppm.

Three series of tests were conducted to examine the temperature dependence of absorption, temperature dependence of desorption and pressure dependence of absorption. The results as well as additional information on test conditions are given in Figure 13 to Figure 15. To facilitate examination of the temperature and pressure sensitivities, the *effective capacity* after two hours of testing was extracted from the reaction kinetics curves and plotted in these graphs. From this, we can see that the 3.3% ScCl_3 +2% Na_2O composition performs well at low temperature absorption and low pressure absorption, but not for low temperature desorption. We also confirm the balanced performance of the 4% TiCl_3 composition.

Figure 13: Temperature dependence of absorption capacity after 2 hours under 68 bar charging pressure for the studied catalysts.

Prototype 1 Media Studies

Figure 14: Desorption temperature dependence for various catalysts.

Figure 15: Absorption pressure dependence for various catalysts.

Prototype 1 Media Studies

3.3.2 Reaction Kinetics Modeling

A detailed description of the reaction kinetics model is given in the appendix of Section 11.1 and has been communicated in Publication 4 of Section 8. This modeling approach tracks the reactions with three state variables that represent the extent of reaction using the three compositions C_1, C_2, C_3 :

The values of the three C_j range between 0 and 1 with the sum of all three being exactly 1.

The reaction rate equations are given by the general form of

$$\left(\frac{dC_j}{dt} \right)_{r_i} = D_i \exp\left(-\frac{E_i}{RT}\right) * \left(\frac{P_{e,i} - P}{P_{e,i}} \right) * (C_k)^{\chi_i}$$

with specific versions given in Section 11.1. See Table 15 for a description of the four directional specific reaction r_i .

To calibrate the model, data from kinetics experiments on material catalyzed with 4 mol % TiCl_3 were compiled. Fitting of the model to this data is shown in Figure 16 with the associated parameters given in Table 5. This model was used in preliminary thermochemical finite element simulations, both steady state and transient, discussed in Section 4.2.3.1.

Figure 16: Comparison of kinetics model and experiment for absorption data at 68 bar and temperatures ranging from 80 to 140°C for 4mol% TiCl_3 material .

Prototype 1 Media Studies

Table 5: Model parameters to fit data in Figure 16.

$(\Delta H/R)r_2$	-6150	Slope in van't Hoff plot, r_2
$-(\Delta S/R)r_2$	16.22	Intercept in van't Hoff plot, r_2
A_2	1.50E+05	Pre-exponent coefficient for r_2
E_2	70	Activation energy for r_2 , KJ/mol of H_2 for r_2
χ_2	1	Reaction order for r_2
$(\Delta H/R)r_4$	-4475	Slope in van't Hoff plot, r_4
$-(\Delta S/R)r_4$	14.83	Intercept in van't Hoff plot, r_4
A_4	1.00E+08	Pre-exponent coefficient for r_4
E_4	80	Activation energy for r_2 , kJ/mol of H_2 for r_4
χ_4	2	Reaction order for r_4

3.4 Cyclic Evaluation

3.4.1 50 Gram Test Apparatus

At the time when this project started, commercially available Sievert's devices were not at the more advanced state that they are today. Due to this and the need to have a readily adaptable system for conducting a variety of non-standard testing, an in-house apparatus was designed and constructed. The apparatus was named the "50 Gram" system because of its ability to test up to nominally 1 kg of hydride or approximately 50 grams of stored *hydrogen*. However, it was more typical to perform tests on sample sizes in the neighborhood of 50 grams of *hydride*. One type of test conducted on this system described in the next section was the evaluation of catalyzed $NaAlH_4$ over multiple absorption / desorption cycles. Other tests performed with moderately large quantities of hydride included evaluation of hydride thermal properties, heat conduction enhancement properties, sub-scale component behavior and Prototype 2 system performance.

The system hardware is shown in Figure 17 (a) which consists of a walk-in hood, computer controlled valves, multiple scale gas accumulator volumes, vacuum pump, oil bath / temperature control, oil pump as well as three pressure and sixteen temperature sensors. Parr reactor vessels of a number of sizes were used as the basis for many of the test articles. Hydride temperature could be controlled either by immersion of a test article into the oil bath or pumping of oil through tubing running within the reactor vessel. The apparatus was controlled by a computer outfit with LabVIEW boards and software. A set of LabVIEW programs was written to control the system manually and/or automatically as well as perform data acquisition. Figure 17 (b) shows the front panel used for manual control in which each of the numbered control valves can be opened or closed by clicking the cursor on the corresponding black rectangle. Automatic pressure establishment and cycle operation were also developed.

Prototype 1 Media Studies

Figure 17: 50 Gram test apparatus; (a) Walk-in hood containing apparatus hardware; (b) Front panel of LabVIEW control and data acquisition software.

3.4.2 Cyclic Test Data

In order to evaluate the cyclic durability of catalyzed NaAlH₄, a number of experiments were conducted on material with compositions containing 6% TiCl₃, 3.3% ScCl₃ + 2 % Na₂O and 6% TiF₃. The tests were conducted using commercial purity NaAlH₄ having the composition breakdown given in Section 3.3.1. The material was prepared by SPEX ball milling the precursors for 3 hours in batches of 10 grams. For all tests, between 36 and 50 grams of material were placed inside of a 200 ml Parr reactor that was immersed in oil having a nominal temperature of 100°C. A thermocouple was located at the center of the powder for monitoring. The hydrogen used was standard purity of 99.95% with typical contaminants being N₂, O₂, H₂O, CO, CO₂ & CH₄. The starting charging pressure was 100 bar and discharge pressure of 2 bar, with changes of typically 2 to 4 bar during the test segment depending on the material capacity. The duration of the charge and discharge steps varied for the different compositions depending on the material's kinetics.

For the 6% TiCl₃ composition, 50 g of hydride powder were tested with 6 hour charge and 6 hour discharge durations. An example of the running pressure data, focusing on the desorption steps is given in Figure 18. Figure 19 plots the pressure results for several cycle counts overlaid on top of each other, showing the reduction in final capacity but little discernable change in the initial kinetics. The pressure change during desorption was converted to hydrogen mass, then weight percent and plotted versus cycles in Figure 20. From this we can see roughly a 10% decrease in capacity after 20 cycles, and the capacity loss rate appears to have decreased after 15 cycles.

For the 3.3% ScCl₃ + 2 % Na₂O composition, 50 grams of powder were tested with 8 hour charge and 24 hour discharge durations. The results in Figure 20 show a 25% degradation of capacity with an apparent slowing of the deterioration near the end of testing. Comparison of the cyclic test curves with data from previous tests on a 1 gram sample having different testing conditions is shown in Figure 21. The change in test conditions, 0 bar pressure and 150°C desorption in particular, and/or processing of larger quantities (10 g per batch rather than 1 g) led to significantly different kinetics.

Prototype 1 Media Studies

Figure 18: Cyclic data for the 6% TiCl_3 composition focusing on the desorption pressure range.

Figure 19: Overlaid desorption pressure data for the 6% TiCl_3 composition.

For the 6% TiF_3 composition, 36 grams of powder were tested with 6 hour charge and 18 hour discharge durations for 37 complete charge / discharge cycles. The results in Figure 20 show greater than a 35% degradation of desorption capacity, which is more significant than for the other compositions.

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Figure 20: Cyclic capacity data taken from the desorption curves.

Figure 21: Overlaid absorption and desorption wt% data for the ScCl₃ + NaO₂ composition.

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4 Prototype 1 System Studies

4.1 Overview

The storage system which contains the CCH powder must serve two primary functions: (1) exchange heat between the powder and a heat transfer liquid to drive the absorption/desorption reactions; (2) support elevated hydrogen pressure during refueling. These functions must be performed with a minimum of weight, volume and cost. In addition, there are other secondary characteristics such as (i) allow for significant volumetric change of the powder, (ii) exchange of hydrogen without the loss of the fine CCH powder particles, (iii) maintain chemical compatibility with the CCH powder and hydrogen and (iv) produce minimal impurities going to the PEM FC. Figure 22 illustrates the various performance goals and design elements associated with system development. An optimal design must consider the various trade-offs associated with the primary components. For example, the heat exchanger sizing must balance the benefit of improved charging time / capacity with increased weight. If pursuing more than just a “paper system”, the non-trivial details of fabrication must be considered and compromises made in the design to be able to construct prototypes with reasonable levels of investment in supporting hardware.

Figure 22: Schematic of performance goals and design elements for system development.

4.2 Prototype 1 Design

Development of metal hydride based hydrogen storage systems dates back several decades with many designs in the journal and patent literature. The complex hydride NaAlH_4 has several significant differences from conventional metal hydrides such as LaNi_5 as listed in Table 6. The higher required charging pressure and lower volumetric density drive the use of a higher performance pressure vessel than conventional stainless steel. The lower volumetric density and lower expansion forces motivate the development of enhanced methods for powder densification and loading. Finally, the high level of water reactivity strongly encourages the use of a non-reactive fluid for heat transfer within the system.

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Table 6: Comparison of design elements for a conventional metal hydride and NaAlH₄.

	LaNi ₅	NaAlH ₄
Charging pressure	10 bar	100 bar
Media volumetrics	50 kg H ₂ / m ³	25 kg H ₂ / m ³ **
Powder loading	Controllable	Challenging
Expansion forces	High	< 7 bar, < 0.9 g/cc
Water reactivity	Low	High

** 50% powder relative density, 4% H₂ media capacity

For both typical conventional metal hydrides and NaAlH₄, the thermal conductivity of the hydride powder is low, and heat conduction through the powder can be limiting. Compared with aluminum, $k_{\text{NaAlH}_4} \approx 0.0025 * k_{\text{aluminum}}$. Thus, the heat transfer challenges are similar, although the sluggish kinetics for NaAlH₄ does reduce the heat exchanger performance requirements if choosing to optimize the heat exchanger to these kinetics.

The overall approach used in the system development is diagrammed in Figure 23. Design concepts were analyzed with a combination of high level and detailed models using inputs from pressure vessel codes, component scaling and experiments. Use of modeling having different detail levels was very beneficial to have both high fidelity when needed and viability for inclusion of broad effects.

Figure 23: Approaches used in the system development.

A diagram of the final design for Prototype 1 is given in Figure 24. This was developed using the considerations and design methods detailed below. In particular, a carbon fiber composite vessel was used, but concerns over the challenges for adequate powder densification motivated a design with a fully opened end vessel so that the aluminum foam disks could be loaded before being installed into the vessel. This approach was also influenced by the additional challenges associated with the large size of the system, being nominally 1 kg H₂ or 25 to 30 kg of catalyzed NaAlH₄.

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Figure 24: First prototype and listed components.

4.2.1 System Scaling Model

One of the first high level models was developed to answer the question: “Given the metrics of a system containing powder 1, what are these metrics for a similar system containing powder 2 with different properties?”

This was of interest for a number of reasons:

1. Understanding how systems designed for conventional metal hydrides will perform using NaAlH_4 .
2. Estimating how improved complex hydride materials will affect system level metrics (for example improving material capacity from 5.5 wt% to 7.5 wt%).
3. Considering subsequent substitution with another material.

These scaling relationships are less detailed than even other high level models developed in the project, but are nonetheless useful for understanding how powder and system performance metrics interrelate. One important, though perhaps obvious conclusion, is that powder volumetrics significantly impact system gravimetrics, i.e. low density powder requires a large pressure vessel which increases system weight.

The model equations are derived in the appendix of Section 11.2. Using the scaling relationships, Figure 25 shows the gravimetric efficiency of configuration 2 using a Savannah River National Laboratory (SRNL) storage system design based on LaNi_5 as configuration 1 and assuming the two hydride powders have the same volumetric densities. An example observation is in order to achieve a 3 wt% system for the scaled configuration 2 ($G_2 = 0.03$) with roughly a 7 wt% material ($w_{p2} = 0.07$), then the gravimetric efficiency of the baseline configuration 1 must be 80% ($W_1 = 0.8$). Thus the gravimetric efficiency of configuration 2 would be reduced to $W_2 = 0.03 / 0.7 = 0.43$, due primarily to the assumption that the volumetrics of the powder are the same for both configurations (in some cases, high wt% capacity materials actually have *lower* volumetrics).

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Figure 25: Configuration 2 gravimetric efficiency using an SRNL design as configuration 1.

4.2.2 Pressure Vessel Design

The pressure vessels for many conventional metal hydride systems have been constructed from 300 series stainless steels (typically 304L or 316L). To estimate the mass of such vessels for higher pressures required to charge NaAlH_4 , the design procedures of the ASME Boiler & Pressure Vessel Code, Section VIII were used. The required mass was prohibitively high, prompting the examination of lighter weight vessel materials. For carbon fiber composite, initial estimates of pressure vessel mass were obtained by gathering performance data for a number of different commercially available vessels. The results for the overall system gravimetric efficiency, including estimates for the heat exchanger and other component masses, comparing these two vessel materials are shown in Figure 26. At pressures in the neighborhood of 10 atm that are typical of some conventional metal hydride systems, the benefit of carbon fiber composite is not significant. However, as expected, at higher pressures around 100 atm needed for NaAlH_4 , the difference is substantial, quantitatively motivating the application of a carbon fiber vessel.

Pressure vessels constructed of aluminum were also considered. Using moderate strength aluminum alloys, the performance is comparable to that of stainless steel vessels. High strength aerospace grade alloys can result in a moderate improvement. The use of extruded aluminum to provide interior reinforcement structures was also considered, which would be an advantage in producing more conformable vessel shapes. The NaAlH_4 is reactive with aluminum, although having an excess of aluminum in the commercial purity NaAlH_4 that is a fine powder with no oxide layer would minimize any degradation of the pressure vessel wall. However, due to the lower performance of aluminum, manufacturing complexity, safety concerns and the desire to use an approach with even higher pressure capability (≈ 200 bar), the vessel was constructed from carbon fiber composite.

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Figure 26: Comparison of stainless steel and carbon fiber composite for pressure vessel performance.

The vendor selected from a field of 25 was Spencer Composites Corporation based on their experience with non-conventional vessel design and high temperature resin filament winding. The required specifications for the vessel were:

- Maximum operating pressure of 1500 psi
- Temperature rating of 250°C
- Minimum of 500 pressure cycles
- Fully open end

As mentioned above in Section 4.2, the vessel was chosen to have a fully opened end so that the aluminum foam disks of the heat exchanger could be loaded with hydride prior to assembly. The maximum temperature that NaAlH_4 can produce at 100 bar hydrogen charging pressure is less than 200°C, but a requirement of 250°C was specified to be conservative.

The vessel was designed by Spencer Composites according to NGV2 specifications with a minimum ambient burst pressure of 4500 psi to guarantee a 2.25 service / burst factor capability at the operating temperature. Finite element analyses were conducted for the domed end, center cylinder section and trap fitting of the open end. Representative results for the trap region are shown in Figure 27. The additional safety margins above a 4500 psi burst pressure based on fiber tensile strain for each major region are

- Dome: 65%
- Cylinder: 23%
- Trap fitting: 103%

The result is a minimum predicted burst pressure of $1.23 * 4500 \text{ psi} = 5535 \text{ psi}$ from a hoop fiber failure mode in the cylinder. Liner fatigue analysis was also conducted that predicted a life of at least 22,000 cycles for temperatures up to 250°C. Thus, the vessel has appropriate amounts of over-design considering that this is a first prototype. Any failure is most likely to occur in the cylinder section, which is desirable since the design methods are most accurate for this relatively simple section, and

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strain gauges give the most consistent readings in this region as well. Three axial and three hoop strain gauges were mounted 120 degrees apart to monitor vessel state both during the vessel hydro proof testing and the storage system performance testing to examine whether any significant hydride powder expansion forces would be generated. Based on data produced by Sandia National Laboratories from Ref. 8, the powder expansion pressure is expected to be below 100 psi for powder densities of 0.9 g / cc or less.

Figure 27: (a) sketch of the trap fitting in the stainless steel liner / flange located at the open end; (b) finite element analysis of the red box region in (a) indicating a maximum axial stress of 100.5 ksi.

The lid for the system was selected to be a commercially available unit produced by the Parr Instrument Company that meets the ASME Pressure Vessel Code. The staff at Parr performed calculations to guide hole positioning as sketched in Figure 24 and ensure that the pressure rating was maintained. As a result of these strength calculations, the locations of the holes near the outer diameter had to be moved inward slightly from the thermally optimum positions.

4.2.3 Heat Exchanger Development

During the discharging of hydrogen, heat must be provided to the NaAlH_4 powder in order to release hydrogen, and during charging, heat must be removed rapidly to keep the temperature down so that the equilibrium pressure is adequately below the charging pressure of 100 bar. However, the powder has a very low thermal conductivity which is on the order of 1/400th that of aluminum. Different types of heat transfer enhancements were considered to improve thermal conduction from the heat exchanger tubing to the storage material. Low density, open-celled aluminum foam was selected due in part to its successful use by Savannah River National Laboratory in conventional metal hydride systems. Advantages of such foam material are its fine structure which reduces the distances over which heat must travel through the hydride, low density strength and convenience in fabrication. Analytical and numerical models were constructed and experiments performed to evaluate the heat transfer performance associated with the metal foam based heat exchanger.

4.2.3.1 Thermochemical Finite Element Modeling Development

The finite element code ABAQUS was selected to perform detailed thermal and chemical simulations because of the ability to customize the calculations in user defined functions and scripting capabilities to automatically evaluation thousands of design points. These simulations were useful to understand

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the full transient behavior and uniformity of the reactions, guide modeling simplifications and interpret experimental results.

The reaction kinetics model described in 3.3.2 were coded in FORTRAN within the user subroutine HETVAL, which determines the heat source/sink magnitude as well as explicitly integrates the evolution equations for the three composition state variables which are stored as “solution dependent state variables”. Due to the high charging pressures, relatively slow reaction kinetics and typically low powder densities of the NaAlH_4 material, the pressure was modeled as spatially uniform but time varying and was prescribed by an ABAQUS “field variable”.

Results from an example absorption simulation are shown in Figure 28. This approach used three dimensional solid elements to model a two dimensional vessel cross section having four passes of heat exchanger tubing through the NaAlH_4 powder / metal foam region. Initially, the vessel is at 80°C and when time = 0, a heat transfer liquid at 100°C flows through the tubing, resulting in a convection coefficient of $5000 \text{ W/m}^2 \text{ C}$. Hydrogen pressure of 100 bars is also applied at this time. Initially, the liquid serves to warm the fully discharged hydride powder, but as the exothermic charging reaction progresses, the powder temperature surpasses 100°C , and the liquid cools the powder. Figure 28 (b) gives the time history plot of the compositions at two points in the cross section. Recalling from Section 3.3.2 that C_3 is the fully hydride composition, NaAlH_4 , and C_2 is the intermediate composition, we see that the charging of point B lags that of point A due to the distance from the heat exchanger tubing and associated temperature rise (not shown) which increases the equilibrium pressure and decreases reaction kinetics.

Figure 28: Example absorption simulation during ABAQUS modeling development; (a) heat exchanger cross section; (b) composition time history for two locations.

Another example set of simulations is given in Figure 29. A 9 inch diameter vessel with 4 wt% aluminum foam starts with fully discharged hydride at 80°C and is subjected to 120°C liquid flow and 100 bar H_2 pressure. The influence of the number of tubing passes was examined, adjusting the diameter of the tubing such that the summed cross sectional area of all tubes was constant. The mass

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of hydrogen absorbed versus time is plotted in Figure 29 (a). As expected, increasing the number of tubes is more effective at removing heat and maintaining the hydride temperature to produce faster reaction kinetics.

Figure 29: Finite element simulation study examining the influence of the number of heat exchanger tubing passes on refueling time.

ABAQUS simulations were also used to iteratively deduce thermal properties from experiments described next that were conducted with the 50 Gram apparatus.

4.2.3.2 Thermal Property Measurement

A number of experiments were conducted to determine the following thermal properties:

1. Hydride powder thermal conductivity (calculated from thermal diffusivity)
2. Aluminum foam thermal conductivity
3. Thermal contact resistance between aluminum foam and stainless steel tubing

The hardware and test article to measure hydride thermal conductivity are shown in Figure 30. Hydride powder is loaded between $\frac{1}{2}$ " and 2" diameter stainless tubing having Teflon end caps. Six very fine type K thermocouples were constructed from 0.003" diameter wire with 0.010" diameter Teflon insulation by tying a square knot in the stripped ends. This unconventional technique was very effective in producing a strong connection that could hold up to tension compared with typical spot welding or torch melting. Keeping the thermocouples as small as possible and orienting them axially as shown in the figure minimized their influence on the temperature field. During the test, the hydride starts off at ambient temperature. Oil that has been preheated is forced down the $\frac{1}{2}$ " tubing and returns through in inner section of $\frac{3}{8}$ " tubing. The temperature histories of the $\frac{1}{2}$ " tubing and hydride at three radial locations are recorded.

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Figure 30: Test article configuration for powder thermal conductivity measurement.

Figure 31: ABAQUS simulation of hydride powder conductivity experiment.

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An axisymmetric ABAQUS model was constructed as shown in Figure 31. The measured temperature history for a thermocouple spot welded to the outside diameter of the ½” tubing is input to the finite element model as a specified boundary condition. Iterations were made for the hydride thermal conductivity, comparing the three measured hydride temperatures. The results from one of the experiments are shown in Figure 32, indicating remarkable agreement with a thermal conductivity value of 0.5 W / m C.

Figure 32: Comparison of experiment and simulation for three hydride thermocouples in the powder conductivity tests. The “TC input” is located on the ½” tubing outside diameter.

A similar approach was used to evaluate the thermal conductivity and thermal contact resistance of the aluminum foam. A foam puck, shown in Figure 33 (b), was pressed onto the ½” diameter stainless steel tubing. The foam was instrumented with the same 0.003” thermocouple wire used in the powder conductivity tests by tying the thermocouple wire to the foam ligaments and measuring the junction radial positions. A reasonably accurate formula for the thermal conductivity of low density foams is

Equation 1

$$k_{foam} = \frac{\rho_{rel} * k_{Al}}{3}$$

where ρ_{rel} is the relative density of the foam or 0.04 in this case. The factor of 1/3 arises because on average only one out of three foam ligaments is parallel to the direction of the heat flux vector for an isotropic foam. The ligament components in the two orthogonal directions do not contribute to long range heat transport. Using this estimate for the foam thermal conductivity but no thermal contact resistance, the poor agreement between the ABAQUS model and experiment is shown in Figure 33 (a). Adding thermal contact resistance, which is represented as the reciprocal of a parameter similar to a convention heat transfer coefficient, good agreement is obtained as plotted in Figure 33 (c) using

$$\frac{1}{h_c} = \frac{1}{500 \text{ W/m}^2 \text{ C}}$$

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The good agreement also confirms the acceptable accuracy of the formula in Equation 1 for foam thermal conductivity.

This experiment was repeated with a test article that had NaAlH_4 powder settled into the foam. In this case, the thermal contact resistance decreased by a factor of 2 to

$$\frac{1}{h_c} = \frac{1}{1000 \text{ W/m}^2 \text{ C}}$$

due to improved thermal coupling caused by the powder as it filled gaps between the tubing and foam ligaments and increased effective contact area.

Figure 33: Determination of thermal contract resistance between tubing and foam through comparison of experiment (solid lines) and simulation (dashed lines). The legends give the radial positions of the fine scale thermocouples in inches.

4.2.3.3 Heat Transfer Fluid Selection

It is most likely that in efforts to maximize convective heat transfer in flow through the heat exchanger tubing, we would encounter a limit regarding how rapidly the heat transfer liquid can be circulated. This may depend on the size and cost of the pump as well as on the energy required to operate it. Quantification of this effect is addressed in this section and a Figure of Merit for heat transfer fluids, termed the Convective Efficiency, is determined. Details of the derivation are given in Section 11.3. The result is the relationship

$$\eta_h = \frac{h * A}{\dot{W}} = \frac{\text{heat transfer per deg}}{\text{pumping power}} = 0.582 * \left(\frac{\rho^{0.05} k^{0.65} c_p^{0.35}}{\mu^{0.70}} \right) * \left(\frac{D_h^{0.05}}{V^{1.95}} \right)$$

The parameter group inside the first set of parentheses involves properties of the heat transfer fluid.

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The Convective Efficiencies for various heat transfer fluids, using a hydraulic diameter = 0.01 m and flow velocity = 1 m/s, are plotted in Figure 34. Water is far superior to any oil but cannot be used due to its high reactivity with NaAlH_4 as shown in Section 3.1.5. Of the high performance heat transfer oils examined, Paratherm MR was the best. This oil also has the desired attributes that it is highly resistant to water absorption, non-toxic and can be used at temperatures up to 280°C.

Figure 34: Comparison of convective efficiency for various heat transfer fluids for a hydraulic diameter of 0.01 m and velocity of 1 m/s.

4.2.3.4 Heat Exchanger Optimization

Given the uncertainties and variabilities in reaction kinetics and operation transients for a storage system, the heat exchanger design for the first prototype was optimized by focusing on the important absorption step for which heat exchange is more rapid and modeling this process as quasi steady state. The latter approximation is reasonable considering that the reaction curves in Figure 16 are linear for the majority of the initial section, resulting in a nearly constant heat generation rate. Based on transient FEA analyses, if the hydride in the storage system is initially above a moderate temperature such as 80°C, the reaction kinetics will be rapid enough to establish the quasi steady state temperature distribution quickly. However, if the storage system starts the refueling operation colder, then it will take 5 minutes or more (See Figure 120 below) for the storage system to reach a point where the quasi steady state (but still temperature dependent) reaction rates are established.

Thus, while transient and steady state FEA were used to evaluate approximations and in some cases determine adjustment factors, the primary calculations were based on the heat transfer network drawn

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in Figure 35. The numbered heat transfer resistances are associated with the following phenomena and resistance formulas:

1. Hydride conduction: $R_1 = \frac{\ln(r_o / r_m)}{2\pi Lk}$
2. Contact resistance: $R_2 = \frac{1}{h_c(2\pi r_m L)}$
3. Wall conduction (minor resistance): $R_3 = \frac{\ln(r_m / r_i)}{2\pi Lk_{tube}}$
4. Heat transfer fluid convection: $R_4 = \frac{1}{h(2\pi r_i L)}$

Note that the length, L , normal to the cross section plane has identical influence for each resistance and could, in effect, be eliminated from the equations, and thus it is not a design variable for this optimization. It was found that given a practical, common range of tubing diameters and circulation velocities, that the heat transfer fluid temperature differed by less than a few degrees Celsius from inlet to exit, further supporting that tubing pass length is not an important design variable for the heat exchanger optimization.

In the calculations, the material was characterized by temperature dependent effective hydrogen capacity and was allowed to have variable kinetics to meet the examined refueling time. In this way, the heat exchanger design was independent of reaction kinetics, so that the design would be based on an absorption scenario that was thermally limited, not kinetically limited, thus being applicable to multiple materials. In the modeling, a number of constraints were imposed. One was to limit the heat transfer fluid circulation and associated convective heat transfer coefficient so that the pumping power was 1% parasitic loss relative to the lower heat value of hydrogen, 120 MJ / kg.

From Figure 36, we see the trade-off between refueling time and system gravimetric performance. This is due to the increased heat exchanger mass needed to maintain adequate hydride temperatures during decreased refueling times. Each marker point in this figure represents a different heat exchanger design for the aluminum foam density, number of tubing passes and tubing diameter. The points on the convex hull, represented by the blue line, are potentially optimum design points depending on the relative merit of weight versus refueling time. The subset of design points on this frontier for a subsequent set of simulations is plotted in Figure 37. The baseline values of the three design variables are given in the graph heading, and the variable multipliers are plotted. Note that the number of tubing passes has been fixed at 24, and we see curves for the optimum values of foam density and tubing diameter as a function of refueling time. As mentioned above, the temperature dependence of the NaAlH_4 effective capacities was included but the kinetics were allowed to vary associated with the specified refueling time. To be conservative, if we select a heat exchanger design for a 15 minute or 900 second refueling time, from Figure 37, this corresponds to all variable multipliers being close to 1 and the optimum design is 24 tubing passes, foam density of 0.04 or 4% and tubing diameter of 0.375" or 3/8".

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Figure 35: Heat transfer network used in combination with ABAQUS FEA to develop the optimum heat exchanger design for Prototype 1.

Figure 36: System gravimetric density versus refueling time for a number of different heat exchanger designs. A convex hull selects the points on the frontier where the optimum design points exist.

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Figure 37: Design variable values for convex hull points. The foam density and tubing diameter are allowed to vary for a fixed number of tubing passes.

While tubing positions could have been optimized through thermal analysis, since this is a second order effect, an approach to maximize the spacing uniformity was applied which also satisfied constraints of having the tubing in the pattern of Figure 38. In this arrangement, the U-tube bend diameters are the same for all pairs and the tube ends are aligned in six rows to simplify the manifolding (See Figure 24). Specific tubing coordinates were calculated using this method and supplied to the vendor of the aluminum foam, ERG.

Figure 38: Tubing positioning in the Prototype 1 cross section.

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4.2.4 Design of Hydride Filter

To support selection of the particulate filters, measurements of mass flow versus pressure drop were made for nitrogen flowing through NaAlH_4 . The relation for flow through porous media given in Ref. 10 was then used to calculate the pressure drop for hydrogen at different flow rates and over different distances. The result was an acceptable pressure drop of less than 4 psi across the powder within the storage system for a two filter configuration and 1 hr discharge of the system. The porous stainless steel filters had an outside diameter of 0.5", inside diameter of 0.25" with a 2 micron grade rating. While there were submicron sized hydride particles, the 2 micron filter was effective due to the significant 0.125" flow path length and tendency for more restrictive filtration as the filter becomes loaded with powder. Any filter will be somewhat self-cleaning as powder is ejected during high pressure, high flow rate charging. In the event that the filters become clogged with the hydride powder or more likely that the pressure is removed suddenly after charging, the filters have been sized to withstand the full 1500 psi working pressure across the filter wall.

4.3 Cost Modeling

The current section gives a very approximate estimate of system costs based on the Prototype 1 design. More detailed studies were subsequently performed by other researchers in the DOE Systems Analysis portion of the Hydrogen Storage Program. For the current effort, cost estimation databases, which have been applied at UTRC in other projects, were considered for the hydrogen storage system, but these tools were considered to be too simple. They took as input only the class of heat exchanger and its volume with a few other categorizing features. This was not considered to be adequate, because the present system is neither a conventional heat exchanger nor pressure vessel. Therefore, the approach used was to obtain cost estimates for the system components and add an additional 30% for manufacturing costs. Since most suppliers could not accurately quote for the large production rate of 1,000,000 units per year, the Theory of Learning was applied to extrapolate quotations to larger quantities. In this basic theory, the cost for a single unit, C_1 , is reduced by the factor $Q^{\log L / \log 2}$ where Q is the quantity, to produce the cost estimate:

Equation 2
$$C = C_1 * Q^{\log L / \log 2}$$

If the quotation or estimate is for an intermediate quantity greater than one, the appropriate form is,

Equation 3
$$C = C_{\text{int}} \left(\frac{Q}{Q_{\text{int}}} \right)^{\log L / \log 2}$$

Note that

$$2^{\log L / \log 2} = L$$

so that L , the *learn down rate*, is the cost reduction multiplier when the quantity is doubled.

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Typical values of L are

- 0.93 to 0.96 for raw materials
- 0.85 to 0.88 for purchased parts
- 0.90 for repetitive welding

according to Ref. 11.

Detailed calculations of the component costs are given in the appendix of Section 11.4 which are summarized in Table 7. The system cost is estimated to be between 400 and 800 \$ / kg H₂ with a 2007 DOE target of 200 \$ / kg H₂.

Table 7: Estimated costs for a production rate of 1,000,000 systems per year.

Component	Cost, low	Cost, high
Composite vessel	\$300	\$600
Heat exchanger tubing	\$80	\$160
Particle filter	\$45	\$135
HT enhancement	\$90	\$90
Valve & PRD	\$20	\$50
Heat transfer oil	\$15	\$25
Water/oil HX	\$30	\$30
Oil pump	\$30	\$30
Manufacturing cost	30%	30%
System hardware	\$793	\$1,456
Hydride	\$1,250	\$2,500
System total	\$2,043	\$3,956
System total per kg H2	400 \$/kg	800 \$/kg

4.4 Storage System / Fuel Cell System Integration Modeling

The objective of this activity was to model and study the integration of a PEM fuel cell system and CCH storage system. The modeling was used to examine system trade-offs, estimate integrated storage system metrics, quantify the significance of integration elements and provide directions for reducing weight and volume.

An existing 75 kW PEM fuel cell model having compressed hydrogen gas as the fuel source was used as the baseline system in this study. It consisted of a PEM stack, Quantum 5,000 psi compressed hydrogen cylinder, pumps, fan, blowers, and Heat EXchangers (HEX). A modified system is shown in Figure 39 where the compressed gas cylinder has been replaced by a CCH storage system with characteristics that were guided by Prototype 1 development. The coolant used in the FC system is water while oil is circulated to remove heat from the water coolant and provide heat to the hydride during desorption.

The variations of the weights and volumes of the HEXs, pumps, blowers and fan were obtained as functions of key sizing parameters. For example, the weight and volume of a HEX is obtained as a function of the hot-side flow rate, hot-side inlet temperature and heat duty. In the case of the pumps, the weights and volumes were obtained as a function of inlet flow rate and compression ratio. A

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software package, HEATS, was used for these sizings. The correlations were used to represent the needed changes in system weight and volume as operating conditions were varied.

The integrated systems were modeled in gPROMS, a chemical systems simulation package. Comparisons of the weights and volumes of the systems are shown in Figure 40 as percentages of the values for the system with a 5 kg H_2 compressed gas cylinder. The system weight using CCH storage is about 35% greater than with the compressed gas cylinder. The increase in the weight is directly attributable to that of the CCH storage device. In contrast, a smaller volume is obtained for the CCH system. To make the CCH system competitive, a reduction in weight is required.

Figure 39: Diagram of automotive PEM FC system integrated with CCH hydrogen storage system.

Figure 40: Comparison of integrated system weights and volumes for compressed gas cylinder and CCH storage. (TMS = Thermal Management System)

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Reductions in weight and volume can be achieved by:

- Technological advancements in the stack design and changing of the operating conditions, which affect the sizes of components in the Balance Of Plant (BOP).
- Improvements in the CCH storage system performance.

The elements studied were:

- (i) Change in operating temperature of the stack (85 to 120°C)
- (ii) Elimination of a HEX by using a common fluid.
- (iii) Improved CCH system with 7.5 wt % capacity, 70% system gravimetric efficiency and 80% system volumetric efficiency

Results of the enhancement studies are given in Figure 41. As before, the weights and volumes are shown as percentages of the total weight of the 5 kg H₂ compressed gas cylinder system. The 5 kg H₂ in CCH system corresponds to the case above before incorporating any enhancements. The *Current Best system* is obtained by increasing the fuel cell operation temperature, resulting in decreased HEX sizes and eliminating the recycle blower through the use of improved stack designs. The resulting reduction in the system weight is less than 10% and is insignificant for the system volume. This is to be expected since this enhancement affects only components that are small contributors to the total system weight. The *2015 Best system* has been computed assuming a better gravimetric and volumetric efficiency for the CCH storage system in addition to the advantages for the *Current Best system*. The baseline CCH system weight and volume were computed using 4 wt % capacity hydride, 50% gravimetric efficiency and 62% volumetric efficiency. The *2015 Best system* estimate is based on a 7.5 wt % material, 70% gravimetric efficiency and 80% volumetric efficiency. The 2015 system achieves an overall reduction in weight of 20% and volume of 45% in comparison to the 5 kg H₂ compressed gas cylinder due primarily to a more efficient CCH device.

Thus, while integration elements do have a secondary influence on the overall system performance, as expected, it is the performance of the CCH system itself that has the primary impact on gravimetric and volumetric performance.

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Figure 41: Comparison of system weights (top) and volumes (bottom) associated with enhancement approaches. (TMS = Thermal Management System; FPS = Fuel Processing System; APS = Air Processing System)

4.5 Prototype 1 Fabrication

4.5.1 Material Synthesis

4.5.1.1 Catalyst Selection

While TiCl_3 is regarded as the standard compound for the introduction of titanium catalysts / dopants, certain data, such as Figure 42 associated with Ref. 12, showed that the anionic species has little influence on the catalytic behavior. During the execution of this project, a sharp rise in the cost of TiCl_3 occurred (due perhaps to increased demand related to hydrogen storage research) as shown:

- August 2001: \$1/g or \$154/mole of Ti^{+3}
- August 2002: \$6/g or \$924/mole of Ti^{+3}
- October 2003: \$12.1/g or \$1860/mole of Ti^{+3}

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To produce the 25 to 30 kg of catalyzed NaAlH_4 anticipated for Prototype 1, just the TiCl_3 alone would have a material cost of over \$30,000. Because of this unanticipated cost increase, the results of Figure 42 and the substantially lower cost for TiF_3 of

- October 2003: \$1/g or \$154/mole of Ti^{+3}

the decision was made to use the TiF_3 form for the Ti^{+3} catalyst. In addition, to achieve more rapid kinetics, a loading level of 6 mole % TiF_3 was selected rather than 4%.

Figure 42: Comparison of TiCl_3 and TiF_3 catalyst forms.

4.5.1.2 Scaled-Up Processing

Scaled up processing with batch quantities of 0.5 kg was pursued with initial procedures using a tumble mill (TM). However, the resulting reaction kinetics were found to be below those obtained for smaller batches produced in a SPEX mill as shown in Figure 43. Here hydrogen wt% is graphed for the 6 mole % TiF_3 composition after the following processing:

- Tumble Milled (TM)
- Tumble Milled plus SPEX Milled (TM+SM)
- Tumble Milled- diluted to 4m% and SPEX Milled (TM+4%SM)
- Tumble Milled plus Proprietary Synthesis #1(TM+1PS)
- Tumble Milled plus Proprietary Synthesis #3 (TM+3PS).

The mechanical energy imparted during these smaller SPEX mill batches was evaluated by measuring the shaking motion utilizing an accelerometer. The accelerometer was aligned along the axis of the milling vials with the resultant accelerations plotted as a function of time in Figure 44. The SPEX milling is seen to impart a 40 g peak acceleration to the milling vials at a frequency of 16.7Hz.

Alternate processing methods were examined and a procedure was developed which improved the kinetics above those produced by subsequent processing with the SPEX mill as shown in Figure 43. The tumble mill alone yielded a high initial desorption rate followed by the lowest capacity after 5 hours. This capacity was considered insufficient for utilization in Prototype 1. The TM+SM processing resulted in kinetics similar to SM alone. Finally, the PS method was developed and found superior to SM. This method was applied to produce the catalyzed NaAlH_4 used in Prototype 1.

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Figure 43: Comparison of catalyzed media processing methods on hydrogen absorption kinetics.

Figure 44: Acceleration measurements of the SPEX mill used to process small batches of hydride. Multiple time traces having different colors have been overlapped.

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4.5.2 Component Fabrication

A number of individual system components were fabricated before system assembly proceeded. The design processes for some of these components have been described in Section 4.2. These components include:

- Hydride material (discussed above)
- Pressure vessel lid
- Composite pressure vessel
- Heat exchanger tubing
- Heat exchanger foam
- Hydrogen port and filter

The pressure vessel lid was based upon a standard Parr Instrument Company design and was modified to have holes with NPT threads for the oil tubes, hydrogen ports and thermocouple instrumentation. A picture of the lid with the 24 heat exchanger tube holes is shown in Figure 45. Once the lid is placed on the vessel, split collars, also shown in Figure 45, are placed over the lid / vessel flanges and tightened. A Teflon gasket on the underside provides effective sealing for hydrogen pressures exceeding 100 bar. After modifications, the lid was subsequently shipped to Spencer Composites to check for fit compatibility with the vessel and to use in hydro pressure testing of the composite vessel as well as of the lid itself.

Figure 45: Parr pressure vessel lid and split collar for Prototype 1.

The composite vessel was fabricated by Spencer Composites Corporation and is displayed in Figure 46, showing the liner with the integrated trap fitting and final state after carbon fiber filament winding. Using the lid, the system was hydro pressure tested to 1.5 times the working pressure of 1500 psi. Then it was pressure tested for an additional 9 cycles to examine whether there were any severe fatigue issues.

Prototype 1 System Studies

Figure 46: Composite vessel: stainless steel liner (top) and carbon fiber wound vessel (bottom).

The 4% dense aluminum foam material was not available as existing stock from the supplier ERG Materials & Aerospace Corporation, requiring specific manufacturing runs. Once the material was produced, the foam disks were fabricated having a thickness of 2", diameter of 9.5" and hole pattern for the 24 tube passes. The tubing for the heat transfer fluid was procured and measured to have a uniform outside diameter of 0.375" $\pm$ 0.0004" which was important to obtain consistent interference fits with the metal foam and minimize thermal contact resistance. Based on previous experiments involving gas flow through the hydride powder, particulate filters were specified by UTRC and manufactured by Chand Eisenmann Metallurgical, Inc. A picture of these three internal components is shown in Figure 47.

Figure 47: Internal components: particulate filter (left); aluminum foam disk (center); heat exchanger U-tube (right).

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4.5.3 System Assembly

As part of UTRC's safety procedures, risk assessments were conducted for both the system fabrication and system testing activities. A list of 27 potential hazards was compiled and mitigations were put in place to reduce the risks to acceptable levels. To support the safe assembly and transport of the storage system, a variety of supporting hardware was designed and constructed. The assembly glove box configuration is given in the sketch of Figure 48 and in the photograph of Figure 49. A stand was needed to hold the vessel during assembly which also served to transport the system approximately 150 meters from the fabrication site to UTRC's Jet Burner Test Stand (JBTS) where the system was evaluated. This stand/cart is shown incorporated into Glove Box #1 in Figure 49 and removed from the glove box in Figure 50. The vessel is permanently mounted to a box frame which can be detached from the cart to facilitate handling with cranes. Prior to assembly, the pressure vessel was installed through the floor of Glove Box #2 as shown in Figure 51 by wire EDMing a tapered section from the glove box which was subsequently replaced and sealed.

Figure 48: Prototype 1 assembly configuration.

Figure 49: System assembly glove boxes and hardware.

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Figure 50: Transportable stand/cart and Prototype 1 system.

Figure 51: Vessel penetrating through the floor of Glove Box #2.

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The assembly process proceeded by first filling the aluminum foam disks with the processed NaAlH_4 hydride in its discharged state within Glove Box #1. Before filling, the bottom and sides of the foam disks were wrapped with aluminum foil to retain the powder. A filled disk is shown in Figure 52. One at a time, each filled disk was passed through to Glove Box #2 and aligned on the heat exchanger U-tubes. Additional hardware was developed to keep hydride powder from entering the heat exchanger tubes and to hold them in position during disk installation as shown in Figure 53. The disks were then pressed onto the tubing, pictured in Figure 54, and pushed down to the bottom of the vessel. For three of the disks located at approximately $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the distance along the length, four thermocouples were installed as diagrammed in Figure 55. The twelve thermocouples were routed along the outside diameter through slots made in the foam disks – see Figure 56, and were subsequently passed through two fittings in the lid.

A total of 17 disks were installed containing 19 kg of hydride. The density of the best disks was 0.6 g/cc while the average powder density within the entire system was 0.44 g/cc, accounting for lower density sections and gaps at the outside diameter, top and where disks could not be pushed completely flush to the disk below it.

Figure 52: Aluminum foam disk filled with nominally 1 kg of hydride powder.

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Figure 53: Removal tubing plugs and positioning supports.

Figure 54: Installation of foam disk onto heat exchanger tubing.

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Figure 55: Thermocouple locations for disk 4 (left), disk 10 (center) and disk 16 (right).

Figure 56: Final disk installation and thermocouple bundle.

Once all disks were installed, the lid was lowered, clamped with the split collars and all fittings were tightened. After cleaning up the glove boxes of excess powder, the vessel was removed and an upper box frame support was attached as shown in Figure 50. The system was then checked for leaks using helium at 1500 psi and a leak detector. Even though the system's filters were pressure tested, secondary filters were also installed on the hydrogen lines at this point to provide additional safety in the event that the primary filters failed. The system was then transported to the JBTS using the integrated stand/cart described above. The long wheel base of the cart not only provided stability to keep the top-heavy vessel from tipping, but also allowed slight flexing to reduce any shock loading to the vessel from bumps.

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As discussed previously, to facilitate the loading and fabrication of this first prototype, a fully open ended design was pursued which added substantial weight to the end closure of the system. The system was constructed with additional factors of safety for both the composite vessel and the heat exchanger tubing resulting in added mass. Also, the powder densities of the final disks were higher than those initially fabricated. Subtracting mass for the heavy end closure and added safety factors, using the powder density of the best disks and adding mass for other components such as supports and insulation, the pie charts in Figure 57 break down the projected gravimetrics and volumetrics for Prototype 1. A gravimetric efficiency of 48% is predicted, which is close to the 50% value anticipated at the beginning of development. As listed in Table 2, the actual gravimetric efficiency was 0.14.

Figure 57: Prototype 1 projected gravimetric (a) and volumetric (b) metrics by component.

4.6 Prototype 1 Testing

4.6.1 Testing Apparatus

Testing of Prototype 1 was conducted in UTRC's Jet Burner Test Stand. This facility offers the safety of 18 inch thick reinforced concrete walls with a blow-out back wall, operation from an external control panel, and technical staff experienced with hydrogen. A diagram of the testing system is given in Figure 58. Pink lines and components denote hydrogen, green is nitrogen, orange is oil and blue is water. In addition to the containment provided by the test cell, a secondary pressure vessel was used shown in green in Figure 58 and in Figure 59 (a). This secondary vessel was purged with nitrogen which then passed through a hydrogen detector to monitor for any leaks.

Mass flow of hydrogen was measured with bi-directional MicroMotion Coriolis force flow meters which are highly accurate and insensitive to temperature or density variations. To cover the wide range of flow rates varying from rapid pressurization or depressurization to the final stages of absorption or desorption that asymptotically approach zero, two flow meters were plumbed in parallel as shown in the lower left of Figure 58 and Figure 59 (b). The oil thermal control hardware consisted of a high power electric heater, cooling heat exchanger, proportional control valve, by-pass line and others, a subset of which are shown in Figure 60.

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Figure 58: Schematic of Prototype 1 testing apparatus.

(a)

(b)

Figure 59: Test stand hardware: (a) containment vessel and (b) hydrogen panel.

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Figure 60: Oil thermal management system.

The test control and data acquisition procedure was developed using an Allen Bradley PLC 5/30 controller and Rockwell Automation Logix 5 PLC programming software. With this system, the operator can monitor and control the test using a 15" touchscreen with the front panel shown in Figure 61 and numerous other sub-panels. Figure 61 also displays the interlock sub-panel where test conditions were monitored for abnormal conditions that would warrant taking corrective actions. One of these interlocks was the H₂ "sniffer" on the nitrogen purge gas which flows through the containment vessel to monitor for leaks in the storage system.

Figure 61: Test stand control software: front panel (left) and interlock sub-panel (right).

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4.6.2 Data Acquisition and Reduction Procedure

Analog data was acquired at a rate of 1 Hz for 40 channels to monitor hydrogen flow rate, pressures, temperatures, strains and test apparatus variables. A second data acquisition system was also used to digitally communicate with the MicroMotion Coriolis force flow meters and eliminate electrical noise pickup during flow rate signal transmission.

A variety of data reduction procedures were developed to concatenate data files, select time ranges, integrate flow rates, perform compressed gas corrections and other functions. Figure 62 shows an example of typical hydrogen flow rate data where initially there is a high flow rate period as the system is pressurized, and then a lower flow rate / constant pressure regime associated with hydride absorption. The flow rate gradually decreases associated with the reaction kinetics. To improve the accuracy of flow measurement as the flow rate continues to decrease, a “burst mode” was developed in which a valve on the hydrogen line to the system is closed most of the time and opened for a fraction of the time to produce bursts of higher flow rates that can be measured more accurately.

To calculate the amount of hydrogen exchanged during either the absorption or desorption reactions, the portion of flow due to compressed gas must be subtracted from the total hydrogen flow measured. An example of the results from this calculation is shown in Figure 63. The “burst flow” approach produces the small steps observed in the “Total measured” curve. The saw toothed shaped “Compressed gas flow” curve is determined from the ideal gas law using pressure data as well as temperature data and free volume measurements. Subtracting the latter from the former results in a surprisingly smooth curve for the “CCH reaction”. By plotting using different axis limits, this process can be seen more clearly in Figure 64 (different test data from Figure 63).

Figure 62: Flow rate and pressure data showing different flow rate regimes.

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Figure 63: Absorption data at 100 bar and 100°C showing the measured hydrogen flow and determination of the absorbed amount associated with solid state reactions.

Figure 64: Smooth reaction curve resulting from burst flow measurement method and data reduction procedure.

To calculate the compressed gas flow, the free volume inside the system must be determined. This was done initially by measuring the flow rate and pressure while filling the system with helium when the hydride powder was in a charged state. The result was a free volume of 33 liters. During absorption testing of a fully discharged material, the calculated absorbed mass curves are given for a range of free volume values in Figure 65. In this figure, the initial 200 seconds involves pressurization from vacuum to 70 bar followed by nominally constant pressure absorption. We would expect these absorption curves to be flat initially and transition to a slope that matches where the pressurization and constant pressure regimes meet. A value of free volume between 34.5 and 35 liters

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gives this consistency. Thus, the testing can resolve that the system experiences a change in free volume of approximately 1.5 to 2 liters due to hydrogen absorption and hydride powder expansion. This represents roughly a 10% change in hydride solid volume over extremes in hydrogen content of about 0.8% weight percent.

Figure 65: Calculated absorbed mass for a number of free volume trial values. The system contained hydride in the fully discharged state.

4.6.3 Prototype 1 Testing Results

Prototype 1 was evaluated under the following pressure and temperature conditions:

Charging

- Standard discharge: 150°C / vacuum / 16 hrs.
- 70 and 100 bar charging (16 hrs):
 - 80°C
 - 100°C

Discharging

- Standard charge: 100°C / 100 bar / 16 hrs.
- 1.5 bar discharging (16 hrs)
 - 90°C
 - 100°C

Data from the first tests indicated that material kinetics and capacities were increasing with cycling due most likely to improved incorporation of the catalyst. Further cyclic testing was then conducted using charge / discharge cycles that could be conducted in a single 8-10 hour workday shift, as shown in Figure 66, to exercise the system in a more time and cost efficient manner. A total of 10 charge / discharge cycles were performed in this manner to stabilize the behavior of the material.

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Figure 66: Cyclic testing with 3 hour segments to stabilize material kinetics.

Subsequently, the longer duration tests, which involved 16 hour segments, were repeated for charging conditions. Results from these charging tests are shown in Figure 67. Initially, hydrogen mass is transferred to the system during the pressurization step. After this, the absorption process takes place having the temperature, pressure and cyclic variations shown. For these conditions, the significance of cycling is comparable to the effect of changing the temperature from 80 to 100°C. The capacity of the hydride material used in the first prototype is approximately 1.0 wt% due to the combined effects of the TiF_3 catalyst and large scale processing methods discussed previously. As seen in Figure 67, the overall capacity of the system is in the range of 0.3 to 0.4 kg.

Discharging test data are shown in Figure 68 for cycles 11 and 12. As before, the material capacities are generally low, and as expected, the reaction kinetics are faster at 100°C compared with 90°C.

Figure 67: Hydrogen mass stored within the first prototype versus time during charging. Cycling has led to improved kinetics and capacity.

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Figure 68: Prototype 1 discharge data; (a) hydrogen mass curves for a 100°C test; (b) material weight percent data at the two test temperatures in the legend.

4.6.4 Prototype 1 Simulations

FEA simulations were performed to compare the interior temperature history measurements with model predictions. Thermocouples were positioned within the system at the locations given in Figure 55. Transient thermochemical simulations were performed using input histories for the hydrogen pressure and heat transfer oil temperature for the charging test of cycle 11 conducted at nominally 100 bar / 100°C. Temperature contours of the vessel cross section are given in Figure 69 for the times and contour ranges described in the figure caption. Since the scaled-up material kinetics/capacity was lower than that used to design the system, the aluminum foam heat exchanger is essentially over designed, and the hydride temperature is quite uniform. Figure 69 (a) shows that the majority of the temperature change occurs through the insulation surrounding the vessel; the simulation time for this plot is when the peak interior temperature occurs at 943 seconds. The contour of Figure 69 (b) is for the same simulation time as (a) but with the lower temperature contour level increased to reveal better the temperature distribution within the hydride. At long times, Figure 69 (c) shows that the temperature distribution is primarily radial due to heat loss at the vessel outside diameter. The time variations of the measured and simulated temperatures are compared in Figure 70. Agreement is reasonable, although the magnitude of the temperature spike is over predicted by the simulation, motivating refinements in the reaction kinetics model. The available thermocouple signal conditioners had an analog resolution of 1°F (5/9°C) which will be improved in future prototype testing.

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Figure 69: FEA temperature contours. (a): 943 seconds, red = 115°C / blue = 50°C; (b): 943 s, red = 115°C / blue = 100°C; (c): 30,000 s, red = 104°C / blue = 96°C.

Figure 70: Comparison of Prototype 1 temperature histories for experiment and simulation. Smooth lines are simulation. Thermocouple locations are given in Figure 55.

4.7 NaAlH₄ Material and System Neutralization

To both safely decommission the first prototype containing 19 kg of NaAlH₄ and to develop more general safety risk mitigation methods, a series of experiments on system neutralization were conducted. This endeavor differs from other material neutralization efforts which focus on the disposal of hydride powder when it is in an easily opened container and can be readily transferred in small quantities. In contrast, our focus was on powders which have been packed within storage systems.

Preliminary tests were conducted on small quantities of hydride powder using an Inel time resolved X-ray diffraction system shown in Figure 71. The powder sample had a starting composition of the

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commercial purity NaAlH_4 described in Section 3.3.1, a thickness of approximately 1 mm and was exposed to ambient air with varying humidity levels. The XRD patterns for various exposure times are given in Figure 72, showing rapid reduction in NaAlH_4 content in the first few minutes followed by slower decreases with the reaction essentially completed after approximately 20 minutes. Figure 73 gives the XRD pattern for the 8 to 9 minute interval where the residual starting reactants of NaAlH_4 and aluminum can be seen, but no crystalline products, such as NaOH , are apparent.

Figure 71: Inel Time Resolved X-Ray Diffraction system.

Figure 72: Exposure of NaAlH_4 (abbreviated NAH in figure) to air at 26°C and 53% relative humidity.

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Figure 73: Composition quantification for NaAlH_4 exposed to air at 26°C and 53% relative humidity for a time frame of 8 to 9 minutes.

Initial tests on 3 grams of surplus material from the first prototype (discharged state) were conducted in which the powder containing Parr reactor was evacuated and then back-filled with humidified nitrogen for tens of cycles. However, even with relative humidity levels of near 100% at ambient temperatures, it is a slow and inefficient process, particularly with manual test operation. The apparatus was modified to have continuous gas flow of humidified nitrogen into a vessel containing 3 grams of hydride, resulting in partial hydrolysis after 48 hrs of exposure. Next, the amount of hydride was increased to 25 g and was loaded within aluminum foam (seen in Figure 33 (b)) which had a filter tube running into the central hole to mimic the first prototype. After 14 days of exposure to a continuous flow of humidified nitrogen, the test vessel was brought back into a glove box that had been emptied of any other materials. The exposed hydride was noted to have changed color and to be deliquescent, i.e. have a paste consistency. Upon carefully removing some of the modified material, it was noted that sections of powder furthest from the filter tube had the original, darker color. A small reaction then occurred for a few seconds which was noted by the production of smoke and heat. From this, we concluded that the water stayed with the deliquescent NaOH, forming a paste which inhibited the transport of water vapor to the corners of the vessel.

To address this, a second gas was added to the humidified nitrogen. A similar test was performed on 25 g of discharged Prototype 1 material. The result was a dry, dark powder similar in appearance to the original material, but unreactive when immersed in water as shown in Figure 74. Additional tests were conducted with a two filter gas flow geometry having 50 g of hydride, still using Parr reactor vessels which can be passed through the glove box antechamber for controlled inspection. These experiments provided additional experience and confirmation before proceeding to larger quantities of material.

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Figure 74: Left – prior water immersion testing of NaAlH_4 from Section 3.1.5; Right – testing of neutralized material indicating no flammability.

To evaluate the effectiveness of the methodology in neutralizing the first prototype, a test with a full scale cross section identical to that of the first prototype was conducted. The unfilled configuration of this test is shown in Figure 75. A surplus aluminum foam disk from the first prototype was split to allow insertion into the vessel. Extra filter rods from the first prototype have also been used for the neutralizing gas inlet and exit. Four thermocouples were positioned 1) near the inlet, 2) near the exit, 3) and 4) at 90 and 270 degrees from the direct gas path between inlet and exit. The test article was loaded with surplus discharged hydride powder from the first prototype using the same vibratory settling method, subjected to the neutralization procedure and evaluated by the water immersion testing at various points in the cross section.

Figure 75: Full scale cross section neutralization test. Left – test vessel; Right – interior of test vessel containing a surplus aluminum foam disk from Prototype 1 and thermocouples.

Two such tests were conducted. For the first test, the flow rate of neutralization gas was approximately 0.6 SLPM (standard liters per minute), and the test was conducted for two weeks. Results from the water immersion tests for samples from various points are shown in Figure 76. The powder near the *inlet* was not adequately neutralized to eliminate flame production during the water immersion tests. This is counter-intuitive. While it is conceivable that the inlet and exit could have

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been accidentally switched, review of the procedure indicated that they were not. Another possible explanation is that the gas sealing at the inlet was not as good as the exit, so that the neutralization gas was able to flow out of plane. Nevertheless, it is still surprising that samples so close to the inlet produced flames. It was also noted that the more completely the powder was neutralized, the harder and more monolithic it became.

Figure 76: Water reactivity results from the first full cross section neutralization trial.

A second full scale cross section test was conducted that was very similar to the first, but with the following changes:

- The gas flow rate was doubled to nominally 1.2 SLPM.
- The 90 degree thermocouple was moved to the center.
- The sealing was improved on the top and bottom surfaces.
- The time was increased to 42 days.
- Humidification of the neutralization gas mixture was stopped intentionally for a day and resumed to see the effects on the reaction through the temperature measurements.

The test temperatures are plotted in Figure 77. Figure 77 (b) graphs the temperature difference relative to ambient and has a logarithmic X axis to better discern the trends. The inlet temperature was significantly higher at the beginning as would be expected. The temperature dropped suddenly when the humidity was stopped and then dropped more slowly, hinting that there may be continued reaction from residual water. The temperature rises when the humidity is turned back on, but not to the previous level. Rather, it appears to reach a level along the subsequent straight line in the log-linear plot. This would also be (partially) consistent with the reaction continuing during the period when dry neutralization gas is being flowed through the disk for one day.

No reactions or hydrogen emissions were noted during the water reactivity tests. A sketch of the sampling locations and test results is given in Figure 78. While the powder became hard, it did not expand significantly. This demonstrated the effectiveness of the approach, though the neutralization is rather slow, this conservatism is desirable for application to Prototype 1.

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Figure 77: Temperature histories for the second full cross section test. (a) Temperature versus time; (b) Temperature difference versus log(time).

Figure 78: Water reactivity results from the second full cross section neutralization trial.

Having established a level of confidence using progressively larger test configurations, the method was applied to Prototype 1 containing 17 aluminum foam disks with approximately 19 kg of discharged NaAlH₄. The prototype was kept within the secondary containment shown in Figure 59 (a) during the procedure. The humidified neutralization gas was flowed through the system at a flow rate starting at 2.5 SLPM and progressively increased to a level of 14 SLPM at 330 hours into the test. The temperature histories for some of the thermocouple locations of Figure 55 are plotted in Figure

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79. The other thermocouples were apparently damaged and not functioning. From the graph, we see the gradual decrease in the heat being released during the neutralization process. When compared with the single disk results of Figure 77, the full system did require approximately 2 to 3 times as long to reach a comparable level of 1 to 2 degree Celsius above ambient. The most likely cause of this is the greater issue for uniform gas distribution with the full length of the vessel. Some locations along the vessel length would have lower gas permeability, in particular the disks with greater powder densification. Based on prior experience, once the material was less than 1 to 2 degrees C above ambient, the material has been neutralized to the point that it will not produce a flame during a water reactivity test. Thus, while the neutralization procedure did require substantial time, it was successfully demonstrated on a number of configurations including the full scale vessel.

Figure 79: Temperature readings during Prototype 1 hydride neutralization.

Prototype 2 Media Studies

5 Prototype 2 Media Studies

5.1 Hydride Processing

Due to the high cost of the TiCl_3 catalyst as discussed in Section 4.5.1.1, $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ was tested as an alternative. This catalyst reacts with NaAlH_4 , forming Ti and Al metal [Ref. 13].

There have been no detailed absorption and desorption kinetics data reported using this catalyst composition. Based on our absorption kinetics studies, increasing Al concentration can enhance absorption kinetics [Ref. 14]. In the development of material for Prototype 2, $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ was tested at doping levels of 2, 2.5, 3, 4, and 6 mol% for both desorption and absorption performance. Our results indicated that the 3 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ doping level demonstrated the best absorption and desorption kinetics and capacity. Figure 80 shows the absorption curves of 3 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ catalyzed NaAlH_4 at $120^\circ\text{C}/68$ bar (a) and the following desorption curves at $100^\circ\text{C}/1$ bar (b) in comparison with those for 4% TiCl_3 and 6% TiF_3 catalyzed materials. All materials were SPEX milled for 3 hours. The new catalyst composition demonstrates better absorption kinetics and capacity than TiCl_3 and TiF_3 . This is probably due to the additional Al content in this catalyst. Its desorption kinetics are inferior to TiCl_3 but it does have higher desorption capacity. It appears that the AlCl_3 in the catalyst enhances absorption kinetics, but hinders the desorption kinetics. Comparing with TiF_3 , it has similar desorption rates, but its capacity is much higher, which is due to a higher absorption capacity prior to the desorption. In order to improve its desorption kinetics and for processing scale up, we investigated processing the material using attrition milling.

In attrition milling, hydride and catalyst are placed in a stationary tank with the grinding media. The hydride and media are agitated by a shaft with arms at high speed which creates both sheering and impact forces on the catalyst and hydride. One major advantage of this processing is that it can be scaled up to produce Ti catalyzed NaAlH_4 in large quantities. High energy SPEX milling can only process up to 10 g of material in each batch. We processed 50 g batches of 3 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and 4% TiCl_3 catalyzed NaAlH_4 , which was done in collaboration with Michigan Technological University. Figure 81 shows the absorption and desorption curves of both materials processed by attrition milling in comparison with corresponding materials processed by SPEX milling. The testing conditions in Figure 81 are the same as those in Figure 80 for both absorption and desorption. For the 3 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ composition, the initial absorption rate of the attrition milled sample is higher than that of the SPEX milled one. However, its absorption capacity is lower than that of the SPEX material. For the 4% TiCl_3 composition, the absorption kinetics and capacity of the attrition milled sample have improved over the SPEX sample. In fact, both compositions have similar absorption performances for the attrition samples. In desorption, the 3 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ composition by attrition milling has faster kinetics and a slightly lower capacity than those by SPEX. Its rate of desorption is approaching that of the 4% TiCl_3 under these test conditions. For the 4% TiCl_3 composition, the attrition milled material has faster desorption kinetics than that of the SPEX sample and the same desorption capacity.

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Figure 80: (a) Absorption curves for 3% TiCl₃·1/3 AlCl₃, 4% TiCl₃ and 4% TiF₃ catalyzed NaAlH₄ at 120°C / 68 bar. (b) Desorption curves at 100°C / 1 bar following absorption at 120°C / 68 bar for 18 hours.

Figure 81: Comparison of SPEX milling and attrition milling for 3% TiCl₃·1/3 AlCl₃ and 4% TiCl₃ catalyzed NaAlH₄; (a) Absorption curves of at 120°C / 68 bar. (b) Desorption curves at 100°C / 1 bar following absorption at 120°C / 68 bar for 18 hours.

When the batch size was increased from 50 g to 100 g, the absorption capacity of the 100 g batch materials was found to be significantly lower than that of the 50 g batch. Specifically, the two hour absorption capacity decreases from 3.61 wt% to 3 wt% at 140°C/110 bar charging conditions as shown in Figure 82. In order to improve the milling effectiveness, hexane slurry milling was investigated. Hexane is an inert solvent to NaAlH₄ and its catalysts. The solvent molecule can improve the milling effectiveness by covering the freshly generated surface upon milling and preventing it from recombining together. It can also decrease the material compaction and adherence to the vessel walls during milling. Small scale hexane milling tests using a SPEX mill produced superior storage capacity and kinetics results over corresponding dry milling and are given in Figure 83.

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To examine scaling up of the promising slurry milling process, NaAlH_4 catalyzed with 3% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ was milled as a hexane slurry using attrition milling by Michigan Technological University (MTU). The primary path for the material processing was for UTRC to perform the drying step, since it was found with our slurry SPEX milling trials that the details on how this is done are important. Nevertheless, drying was also pursued by MTU in which the slurry/paste was placed in two trays and dried under vacuum in the antechamber of the glove box. The trays were then transferred to the glove box main chamber and while hydride powder was being collected using metal utensils, a spontaneous reaction occurred which increased the glove box pressure to the point that a weak spot fractured where holes had been cut in the back window. The event may have been caused by a combination of exposure to air during drying and possible electrostatic spark generation during scraping to collect the powder. The glove box was re-sealed and clean-up was conducted by an approved hazardous materials company. However, a consequence was that this facility could not be used to produce the material for Prototype 2.

Figure 82: Comparison of absorption capacity for 3% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ catalyzed NaAlH_4 processed by attrition milling at 50 g and 100 g batch sizes.

Additional catalysis studies were conducted involving the addition of FeCl_3 to improve the desorption kinetics. Through a number of trials, the composition of 2% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3 + 0.5\% \text{FeCl}_3$ was found to give the best performance. The effective capacity for a range of charging temperatures is given in Figure 84 along with the previous best material involving an alternative catalyst approach. At charging temperatures of 100°C and above, the SPEX milled 2% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3 + 0.5\% \text{FeCl}_3$ was superior.

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Figure 83: Desorption kinetics of $3\% \text{TiCl}_3 \cdot 1/3 \text{AlCl}_3$ catalyzed NaAlH_4 processed by dry SPEX milling and hexane slurry SPEX milling.

Figure 84: Temperature dependent two hour absorption capacity of material candidates.

As mentioned in Section 2.1 and discussed in more detail in Section 6, Prototype 2 was constructed at nominally a 1/8 kg H_2 scale which ultimately involved the loading of 3500 g of catalyzed hydride. As a recovery option due to inoperability of the MTU attrition mill, SPEX milling was used to produce 4000 g of material catalyzed with $2\% \text{TiCl}_3 \cdot 1/3 \text{AlCl}_3 + 0.5\% \text{FeCl}_3$. To improve milling

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effectiveness, the number of milling balls was doubled from that used previously for 2 g batches. Production proceeded by processing 4 vials at a time which were milled for 3 hrs. Adding the 1 to 1 ½ hrs. required to empty and reload the SPEX mill vials, between 2 to 3 milling sessions were conducted per day, producing either 80 or 120 g of catalyzed material per day or approximately 500 g per week. Thus, the production of 4000 g was conducted over approximately a 2 month period during the Prototype 2 fabrication.

The quality for all of the milled material was first checked by sampling individual 10 g batches, then mixing the four batches from the four milling vials used and testing a 1 g sample. With the high level of repeatability observed, 50 batches were mixed together for a number of quality verification tests and finally 150 batches were combined, in each case testing a 1 g sample. Results from the absorption and desorption tests are shown in Figure 85 and Figure 86. Since a limited amount of high temperature epoxy was used in the fabrication of the Prototype 2 heat exchanger, compatibility with this material was verified and is shown in the figures. The absorption data are slightly higher than what is expected or consistent with the desorption data due most likely to inaccuracies in the data reduction procedure (free volume determinations and temperature corrections). However, the consistency from sample-to-sample (individual and mixed batches) is good for both absorption and desorption. In the desorption tests, the temperature is ramped from 100 to 150°C in one hour. The capacity is seen to be reasonably good with a nominal value of 3.5 wt%. Tests were also performed to evaluate the material reaction kinetics after a practice powder filling procedure, described below in Section 5.2, with the results being acceptably consistent.

Figure 85: Absorption quality control testing of prototype 2 material.

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Figure 86: Desorption quality control testing of prototype 2 material.

5.2 Powder Densification

In order to develop the lightest possible system that could provide moderate pressures for charging NaAlH_4 and potentially other novel materials, carbon fiber composite vessels have been utilized in the prototype development. To minimize the heat exchanger mass, an optimized finned tube heat exchanger was developed for Prototype 2 as discussed in Section 6.2. Furthermore, in order to minimize the weight of the composite vessel, it is important to use the smallest possible polar boss (end opening) which requires that the hydride powder be loaded after the composite vessel has been formed around the heat exchanger. The resulting technical challenge to realize such a light weight system design is to develop methods of tightly packing the low density hydride powder inside the finned heat exchanger contained within the composite vessel.

In this project, a powder loading method was developed that is both compatible with pressure vessel / heat exchanger assembly and achieves high powder packing densities. Loading of NaAlH_4 requires significantly more effort than conventional metal hydrides since this material has particles of nanometer size which causes cohesive inter-particle attraction and agglomerations. The first full scale prototype achieved an average powder density of 0.44 g/cc and a peak density of 0.6 g/cc. The goal for Prototype 2 was to develop a superior media filling procedure that increases the average powder density to over 0.7 g/cc.

To support this development, a novel powder densification apparatus was designed and fabricated, which produces vibrations in two orthogonal directions in combination with other densification enhancements. The development of powder densification methods was conducted using three different vessel configurations shown in Figure 87. Vessel (a) has a clear acrylic tube, allowing for

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visual inspection of the densification process, with an interior diameter of 3/8", length of 6" and removable end caps. Tests with this vessel examined the more fundamental characteristics of powder densification for different:

- vibration frequencies and amplitudes
- vibration directions – parallel and perpendicular to the densification axis
- densification enhancement details

These tests provided information on the optimal and near optimal densification conditions to be applied in the other two configurations.

Test vessel (b) contained a stack of fins to develop the loading process within the horizontal inter-fin channels. Two variants of the fin stack were constructed. The first replaced the heat exchanger tubing with threaded rod so that the stack could be disassembled within the glove box to evaluate the powder distribution and densities for each inter-fin channel. The second variant of vessel (b) had normal tubing to be able to test the absorption and desorption rates of the loaded hydride and heat exchanger. Configuration (c) represents the actual Prototype 2, which used similar densification conditions and loading process as those developed with the vessel (b) experiments.

Figure 87: Three configurations used to develop powder densification methods. (a) column of powder; (b) finned heat exchanger which can be disassembled; (c) Prototype 2 carbon fiber composite vessel with heat exchanger.

Two electromagnetic shakers were used to vibrate the test configurations independently in orthogonal directions. For vessel (a), these directions were parallel and perpendicular to the densification axis. For vessels (b) and (c), these directions were perpendicular to and in the plane of the fins, but generally not parallel to the radial densification direction. The shaker apparatus with vessel (a) is shown in Figure 88. Two accelerometers were attached to the test article to measure the intensity of vibration. The signal generators used to drive each shaker could sweep the vibrational frequency as shown in Figure 89. The physical interpretation for this phenomenon is that particle and particle group rearrangement involves a complex and widely ranging distribution of obstacle types that are best overcome with mechanical activation that spans a range of intensities. An example of the limited

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number of related studies in the literature is given in Ref. 15. The current apparatus is unique in providing controlled vibration in two directions along with other densification enhancements.

Figure 88: Apparatus with independently controlled, dual axis shakers set up with powder vessel (a) to examine fundamental powder densification characteristics.

Figure 89: Frequency sweeping from 50 to 300 Hz to promote activation past particle rearrangement obstacles. (amplitude variation is due to shaker characteristics and a minor structural resonance at 0.45 s)

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A variety of materials were examined as both the densification apparatus and the Prototype 2 final material composition were developed. These included alumina powder, surplus material from Prototype 1, 3% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ catalyzed hydride and finally the 2% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3 + 0.5\%$ FeCl_3 material used in Prototype 2. The average crystallite size of the NaAlH_4 powder was determined previously to be $0.05\ \mu\text{m}$ through X-Ray Diffraction (XRD) methods. Although there is extensive literature available on packing of granular materials, there is little research on the controlled densification of nanometer scale powdered materials. To better understand densification behavior, it was useful to measure the particle size distribution. Reactivity of the hydride with oxygen and water vapor excluded traditional methods of particle size analysis, such as Coulter Counters or Laser Diffraction. Through Scanning Electron Microscopy (SEM) we were able to visually determine a particle size range from single $0.04\ \mu\text{m}$ crystallites to $2\ \mu\text{m}$ agglomerations.

In order to perform preliminary testing and apparatus refinement, experiments were performed with an inert surrogate material that could be used in experiments outside of a glove box. The surrogate nano-powder selected was $0.05\ \mu\text{m}$ γ -alumina commonly used in metallographic polishing. Preliminary densification tests were conducted on the alumina powder in the apparatus described above using frequency sweeping. The results are plotted in Figure 90, indicating that vertical vibration, i.e. parallel to the densification direction, is more effective at overcoming particle rearrangement barriers. Also, biaxial vibration is marginally more effective than vertical vibration alone. Comparisons of the alumina with NaAlH_4 for particle size and density are given in Table 8 along with densification results for NaAlH_4 obtained using aggressive manual vibration.

Figure 90: Densification curves for uniaxial and biaxial vibration of $0.05\ \mu\text{m}$ γ -alumina powder.

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Table 8: Comparison of the densification for alumina and NaAlH₄ nano-powders.

	γ -Alumina	NaAlH ₄
Particle Size	0.05 μ m	0.04 μ m - 2 μ m
Theoretical Density	0.5g/cc	1.28g/cc
Density Achieved through Vibration	0.37g/cc	0.75g/cc
Relative Density	74%	59%

After completing preliminary experiments with surplus 6% TiF₃ catalyzed NaAlH₄ from Prototype 1, MTU's attrition milled 3% TiCl₃*1/3 AlCl₃ material was investigated. Densification occurred under just vibration, but higher densities can be achieved with enhanced settling methods. These results are shown in Figure 91. The final densification achieved with the 3% TiCl₃*1/3 AlCl₃ NaAlH₄ of 0.62 g/cc was significantly lower than that obtained with the 6% TiF₃-NaAlH₄ material of 0.75 g/cc. This difference in densification is a result of the processing method and the hydrided state. The 6% TiF₃ material was processed in a moderate energy shaker and subsequently dehydrided whereas the 3% TiCl₃*1/3 AlCl₃ NaAlH₄ was aggressively attrition milled for 6 hours and not thermally dehydrided. This data motivated improving our understanding of the different behavior of dehydrided versus hydrided states on powder densification. Results of this study are presented in Figure 92. It was theorized that densification should increase after dehydriding the material, however results show this is not the case. As the hydride is discharged and recharged, the achievable densification decreases.

Figure 91: Effect of horizontal and vertical frequency sweeping on densification of attrition milled 3% TiCl₃ * 1/3 AlCl₃ material followed by enhanced settling methods.

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Figure 92: Effect of discharge/recharge on densification of attrition milled 3% TiCl₃*1/3 AlCl₃ NaAlH₄ (50 & 100 g batches).

Table 9 presents a comparison between the dehydrated 6% TiF₃ NaAlH₄ and the 100 and 50 gram batches of attrition milled 3% TiCl₃*1/3 AlCl₃ NaAlH₄. As before, these tests used the acrylic tube configuration of Figure 87 (a) which densified a column of powder. The decrease in densification upon discharging and recharging is significant relative to experimental error. It is apparent that the batch size of the attrition milled material has an effect on densification (in addition to the reaction kinetics) with the larger batch size having the lower density.

Table 9: Comparison of densification for various hydride materials including the effect of discharging / recharging.

6% TiF ₃ -NaAlH ₄		3% TiCl ₃ /AlCl ₃ -NaAlH ₄ 6 hrs attrition milled, 100 gram batch			3% TiCl ₃ /AlCl ₃ -NaAlH ₄ 6 hrs attrition milled, 50 gram batch
Processing technique	Paint Shaken	Attrition Milled	Attrition Milled + Dehydrated	Attrition Milled + Dehydrated/Recharged	Attrition Milled
Original Density g/cc	0.462	0.322	0.362	0.351	0.391
Vibratory Settling g/cc	0.740	0.475	0.460	0.430	0.465
Enhanced Settling g/cc	0.751	0.629	0.607	0.555	0.669
	± 0.008	± 0.016	± 0.029	± 0.029	± 0.040

Since the densification achieved with the attrition milled 3% TiCl₃*1/3 AlCl₃ NaAlH₄ powders was significantly less than that attained with 6% TiF₃ NaAlH₄, solid lubricants to facilitate particle rearrangement were explored. Graphite powder was selected as the first candidate. Based on a literature review, two concentrations of the graphite powder were explored, 0.5 wt% and 5 wt%. The

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appropriate quantities of graphite and attrition milled NaAlH_4 , along with a control sample, were SPEX milled for 10 minutes. Densification tests with the acrylic vessel configuration were then conducted on the three powder states, and the results are given in Table 10. Data column 3 shows that SPEX milling of the control sample for 10 minutes resulted in a 33% increase in powder densification from 0.629 to 0.835 g/cc. This result reinforces that milling procedures are important not only to achieve rapid kinetics but also high powder densification. High resolution SEM images of Figure 93 did not show a significant visual difference in particle size or morphology between the attrition milled and SPEX milled powders. The addition of graphite on densification was secondary to the benefits of SPEX milling, and it was decided that additional solid lubrication studies would not be pursued.

Table 10: Densification of SPEX remilled powder to add 0 wt% (control), 0.5 wt% and 5 wt% graphite to attrition milled 3% $\text{TiCl}_3 \cdot 1/3 \text{AlCl}_3 \text{NaAlH}_4$.

	6% $\text{TiF}_3\text{-NaAlH}_4$	3% $\text{TiCl}_3\text{AlCl}_3\text{-NaAlH}_4$	3% $\text{TiCl}_3\text{AlCl}_3\text{-NaAlH}_4$	3% $\text{TiCl}_3\text{AlCl}_3\text{-NaAlH}_4$ - 0.5% Graphite	3% $\text{TiCl}_3\text{AlCl}_3\text{-NaAlH}_4$ - 5% Graphite
Processing technique	Paint Shaken	Attrition Milled (100g batch)	Attrition Milled then SPEX Milled (10 min)	Attrition Milled then SPEX Milled (10 min)	Attrition Milled then SPEX Milled (10 min)
Original Density g/cc	0.462	0.322	0.499	0.481	0.476
Vibratory Settling g/cc	0.740	0.475	0.629	0.639	0.660
Enhanced Settling g/cc	0.751 ± 0.008	0.629 ± 0.016	0.835 ± 0.019	0.835 ± 0.021	0.861 ± 0.019

(a)

(b)

(c)

Figure 93: High resolution SEM micrographs of 3% $\text{TiCl}_3 \cdot 1/3 \text{AlCl}_3 \text{NaAlH}_4$ powder which underwent three different milling procedures. Densities achieved were (a) 0.64, (b) 0.85 and (c) 0.72 g/cc.

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Powder densification tests were conducted for the 2% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3 + 0.5\% \text{FeCl}_3$ material being produced for the second prototype using the powder column configuration. The results indicated that powder densities of 0.72 g/cc can be achieved for this hydride material in the particle size and morphological state produced from the SPEX milling process.

Powder densification of the 100 gram batch attrition milled material was also evaluated using the test configuration shown in Figure 87 (b) for a finned tube heat exchanger. Initial tests were not successful in meeting target densities, resulting in 0.57 g/cc and severe warping of the 0.004" thick aluminum fins as shown in Figure 94.

Figure 94: Sub-optimal attempt to densify hydride in finned structure.

The fins were modified by creating shallow corrugations to increase their structural integrity as shown in Figure 95 (a). These stiffened fins were used in subsequent experiments having modified densification conditions. A maximum density of 0.66 g/cc was achieved in the finned structure shown in Figure 95 (b) which compares well for the column configuration density for the 100 gram batch attrition milled material from Table 10 of 0.629 g/cc.

Figure 95: (a) Stiffened fin used to achieve an average density of 0.66 g/cc in stack (b).

Figure 96 shows a partially disassembled fin stack. The hydride appears uniformly distributed and well packed throughout the fin cross section. In previous tests where lower densification was

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achieved, the hydride flowed easily and slid off of the fins when they were lifted. In this case, the powder remained compacted and adhered to the fins.

Figure 96: Disassembled fin stack of Figure 95 (b) showing uniformity around the tubing regions.

Similar tests were conducted using the 2% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3 + 0.5\% \text{FeCl}_3$ material for Prototype 2 in which the average powder density in the subscale finned structure was 0.77 g/cc which was comparable to the powder column value of 0.72 g/cc.

5.2.1 Application to Novel Materials

The powder densification techniques were applied to novel materials developed in another DOE contract, DE-FC36-04GO14012, to evaluate the volumetrics and powder loading system integration issues for other storage materials. The three additional powders studied along with NaAlH_4 are shown in Figure 97. Data for the material volumetric density is given in Figure 98 in which the powder densities for three conditions are combined with the theoretical H_2 capacity. Note that while $\text{LiMg}(\text{AlH}_4)_3$ has good gravimetric potential, its volumetric performance in the as-synthesized state is low. Additional milling and other processing could improve densification of these powders as was demonstrated for NaAlH_4 above.

Figure 97: Powder samples for three newly developed storage materials along with NaAlH_4 .

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Compound	Theoretical Rev. H ₂ wt fraction	Initial Density kg H ₂ /liter	Vibratory Settling kg H ₂ /liter	Enhanced Settling kg H ₂ /liter
LiMg(AlH ₄) ₃ *	0.089	0.010	0.014	0.019
M-B-N-H System A *	0.088	0.033	0.041	0.042
M-B-N-H System B *	0.082	0.035	0.044	0.044
NaAlH ₄ - best result **	0.056	0.026	0.041	0.042

Figure 98: Volumetric density of three novel storage materials in comparison with NaAlH₄ (theoretical capacities).

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6 Prototype 2 System Studies

Based on the experience gained from Prototype 1, a number of advancements were pursued in the development of Prototype 2. These included:

- Lighter weight end closure for the composite vessel
- Improved heat exchanger performance with the use of fins rather than foam
- Greater powder densification
- Compact oil manifolds

In order to achieve the first and third of these items, an advanced powder loading approach had to be developed as discussed above in Section 5.2. Fabrication using this loading method required biaxial shaking of the entire system. Because this would require substantial resources for shaker sizing, frame development, glove box size and other supporting hardware, the size of the system was reduced to approximately $(1/2)^3 = 1/8^{\text{th}}$ scale. This size allowed existing in-house shakers and power modules to be used as well as a 5' by 5' by 4' glove box for system loading while still demonstrating the technology with only minor extrapolations. A sketch of the Prototype 2 design is shown in Figure 99.

Figure 99: Sketch of the second prototype design.

6.1 Pressure Vessel Design

As with Prototype 1, the pressure vessel was designed by Spencer Composites Corporation. Without the fully opened end and associated trap fitting, the design details followed those for more common types of composite pressure vessels. The pressure and temperature histories used in the finite element analysis are shown in Figure 100. Example FEA results (analysis step 4) are shown in Figure 101. The analysis indicated that the minimum predicted burst pressure for the vessel is 4320 psi at the ambient burst test condition and 3645 psi relative to the hottest service condition. These pressures exceed the design minimum burst pressure of 3375 psi. A hoop fiber failure mode in the cylinder was predicted for both conditions. Also, the liner fatigue life for the service pressure of 1500 psi was greater than 19,000 cycles for temperatures up to 200°C. The liner carries only a small portion of the overall load and a fatigue crack in the liner will result in a non-catastrophic leak before vessel rupture.

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Figure 100: Pressure and temperature histories used in composite vessel nonlinear FEA.

Figure 101: Port dome von Mises stress at the service pressure and highest temperature, 1500 psi & 200 °C.

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6.2 Heat Exchanger Design

6.2.1 Overview

The Prototype 1 heat exchanger used aluminum foam to enhance heat conduction due to the low conductivity of the hydride powder. Aluminum foam has a number of advantages as detailed below, but it also has disadvantages, the most significant of which is the less than optimum thermal conductivity. To address these shortcomings, design of the second prototype involved a finned tube heat exchanger which needed to be designed for optimum heat transfer and to include features for powder loading, while having acceptable durability and ease of fabrication.

Figure 102: Illustration of long range and short range heat conduction.

A summary of the advantages and disadvantages of the two types of heat conduction enhancement are outlined below. To help understand the terminology and heat transfer path, Figure 102 shows the short range heat conduction from the hydride powder to the conduction enhancement and the long range heat transport from the conduction enhancement to the heat exchanger tubing.

Conduction enhancement

- Foam - Pros
 - Fine length scales – good short range heat conduction
 - Good strength for low relative densities
 - Easily incorporated into design
- Foam – Cons
 - 1/3 factor reduction in long range heat conduction (recall Equation 1)
 - Lack of flexibility for powder loading and migration mitigation
 - Cost
- Fins – Pros
 - Good long range conduction
 - Geometric flexibility
 - Cost
- Fins - Cons
 - Must engineer for fine length scales for adequate short range conduction
 - Structurally weaker for given average relative density

Optimization of the heat transfer was performed with modeling at two length scales: low length scale to optimize certain variables and at the full cross section to examine the effect of tubing positioning.

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6.2.2 Low Length Scale Modeling

Because the Prototype 2 heat exchanger (HX) involves fins with lower length scale aspects that can be tailored, it is more important to model the conduction enhancement on this scale than it was for the inherently fine aluminum foam of Prototype 1. Therefore, the FEA simulations supporting this design activity were performed on the scale of a fin unit cell. The design variables were

- fin spacing
- fin thickness
- fin OD (related to the number of tubes)
- fin ID (or tube OD).

In addition, three model parameters were varied from minimum to maximum values to represent cell-to-cell variability which were

- hydride thermal contact resistance
- hydride density
- reaction rate uniformity.

The primary function of the heat exchanger is to maintain an adequately *uniform* temperature throughout the hydride while heat is being removed during charging. A secondary function is to have the hydride temperature be as close as is necessary to the oil temperature for adequate control during charging transients and also to have the temperature be as high as possible using fuel cell waste heat during discharging so that the average hydride temperature can be made as close to the optimum as is needed.

Since during charging, we have some flexibility with the temperature of the cooling fluid, we can tolerate a moderate temperature difference between hydride temperature and oil temperature and that is why this is a secondary and not primary function. How large a difference we can tolerate will depend on consistency of tubing / fin contact resistances from point to point, variation of convective heat transfer coefficient (minor) and on the severity of transient effects – how large is the spike in temperature and how quickly can the oil temperature be changed.

The fin unit cell was approximated as two dimensional, axisymmetric. To justify this, Figure 103 shows results from a cross section model from Prototype 1. This contour plot shows that the temperature variation around each tube is predominantly circumferential and therefore reasonably represented by the axisymmetric model.

Features of the fin unit cell model are labeled in Figure 104 and the extended region for four unit cells is shown in Figure 105. The fin collar height was fixed as 0.5 times the tubing radius as an estimate to what could be formed. For a 0.250" tubing diameter, this would be $0.5 * 0.125" = 0.0625"$. Actual fabricated collar height measured later was 0.040", but sensitivity of the results to this parameter is low once the collar height is above a level of approximately 0.020".

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Figure 103: Temperature contours for a representative steady state analysis of Prototype 1, supporting the approximation of an axisymmetric fin unit cell model.

Figure 104: Single fin unit cell model with example temperature contour plot.

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Figure 105: Periodicity of unit cells.

Baseline values for key parameters are given in the Table 11. The fin thickness of 0.004" is what is commonly used in air conditioners and was the minimum value considered, since thinner fins would be too weak for powder loading. The spacing of 0.2 gives a heat conduction enhancement density of nominally $0.004'' / 0.2'' = 0.02$ or 2% which is half the weight of the 4% aluminum foam used in the first prototype.

Table 11: Baseline values of model parameters.

Variable	Value
Fin spacing	0.2''
Fin thickness	0.004''
Fin outside diameter	1.5''
Fin inside diameter	0.250''
Fin collar height	0.0625''
Refueling time	15 min
Hydride density	600 kg/m ³
Enthalpy	40 kJ/mole
Weight fraction H ₂	0.04
Pressure vessel mass factor	2.83e-5 kg / Pa m ³
Vessel pressure	100 atm
Convective film coefficient	1500 W/m ² C
Oil temperature	80 C
Tube / fin conductance	2000 W/m ² C
Tube / hydride conductance	100 W/m ² C
Fin bottom / hydride conductance	100 W/m ² C
Fin top / hydride conductance	100 W/m ² C
Fin collar / hydride conductance	100 W/m ² C

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An ABAQUS script was developed which automatically built and solved the model for the given parameters, and repeated this for the prescribed matrix of parameter values. The script then processed the full spatial distribution of the hydride temperature and simplified it to store only a volumetric temperature distribution at a reduced number of points as shown in Figure 106. In this curve, we can see that between the 10% and 100% values of the abscissa, that 90% of the hydride powder is between temperatures of about 116 to 122°C.

Figure 106: Temperature fields, such as those in Figure 104, are reduced to a cumulative distribution curve with respect to volume.

In reality, there will be variations in some conditions such as thermal contact resistance and hydride powder density from point to point within the unit cell and from unit cell to unit cell. To capture the latter aspect of the variation, i.e. the cell-to-cell variation, the model was exercised in sequence with different properties and the results combined to produce an overall temperature distribution curve for a collection of unit cells.

In a vertical system orientation, we might expect gravity to produce a higher thermal contact conductance for the top surface of the fin than the bottom surface. When the powder is discharged, we might expect it to pull away from the fin wall, opening up a gap on the bottom fin surface. When the system is horizontal, we would expect the bottom of the cylinder cross section to have a higher density of powder due to settling and also better thermal contact conductance between the hydride and fins. The effect of this variation can be seen in Figure 107 where all four hydride conductances given in Table 11 are given values of either 50, 200 W/m² C or as listed in the legend. If we combined these unit cell results into a distribution for multiple cells representing the entire system, then we would have a significantly wider temperature distribution.

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Figure 107: Sensitivity study for hydride contact conductance with oil temperature of 80°C.

For speed of execution, the ABAQUS simulations were performed only for upper and lower limits of each variable and stored in memory. Then a combined T(V) curve was determined for each set of the four design variables. Using variabilities of

- conductance: +/- 30%
- density: +/- 20%
- reaction rate: +/- 10%

results for the Lower and Upper limit curves are given in Figure 108, where for example “LLL” is the curve using the lower value for each of the probabilistic parameters. The overall curve is shown as a solid red line that represents the temperature distribution for a collection of unit cells.

Figure 108: Responses for Lower and Upper limits of parameters and resulting overall temperature distribution curve.

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As a step in determining the overall capacity of the system, the temperature dependent capacity of the storage material must be specified. At the time of these simulations, data was not available for the alternate catalyst materials described in Section 5.1, so data for the 4 mole% TiCl_3 composition were used. The typical capacity versus time curves at different temperatures have been converted to capacity versus temperature at different times as shown in Figure 109. Conservative levels of 0% were prescribed for 60 and 160°C.

Figure 109: Temperature and time dependence of material capacity.

Another step to determine the overall system capacity is to determine the optimum cooling oil temperature. To do this, an offset from the value used in the ABAQUS simulations was calculated to maximized the average system capacity. The average system capacity was calculated for a given refueling time as

$$w_{avg} = \frac{1}{\tilde{V}_f} \int_0^{\tilde{V}_f} w(T(\tilde{V}) + T_{offset}) d\tilde{V}$$

where $\tilde{V}_f = 1$, but the above form is written to show the nature of the normalization. This was calculated for the discrete number of points for the solid red curve of Figure 108

$$w_{avg} = \sum_i w(T_i + T_{offset}) * \Delta\tilde{V}_i$$

where $\tilde{V}$ is volume *fraction* rather than volume *percentage* as in the plots. A range of oil temperature offsets values, T_{offset} , are tried and the one with the highest w_{avg} is chosen. A limit is put on T_{offset} so that the oil temperature cannot be below a lower limit which was specified to be 20°C. Example original $T(V)$ curves and those with the optimum offsets are shown in Figure 110 and Figure 111 having a reaction rate multiplier of 8 to enhance the kinetics in sensitivity studies.

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Figure 110: Overall temperature distribution curves for each design point overlaid with temperature dependent material capacity data with no offsets to the oil temperature.

Figure 111: Curves from Figure 110 with optimum offsets to the oil temperature.

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For a refueling time of 30 minutes and reaction rate multiplier of 4 to add in conservatism to the heat exchanger design, the results of system capacity versus heat exchanger density for each of the examined design points is given in Figure 112. The values of the design variables, combining the baseline values in the legend with the multipliers read from the graph, are given for each point on the convex hull. By focusing on the region with the peak system capacity, we can identify the optimum design variable values.

Figure 112: System capacity results for all design points of a particular study.

Figure 113: Design variable multipliers for points on the convex hull of Figure 112.

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If we restrict the tubing diameter to be 0.250" for fabrication / procurement reasons, the optimum design parameters from Figure 114 are

- fin spacing = $1.0 * 0.2'' = 0.2''$
- fin thickness = $1.0 * 0.004'' = 0.004''$ (minimum considered in study)
- fin OD = 1.6"
- fin ID = 0.250" (fixed)

with little change in the optimum system capacity.

For the broadest execution of the ABAQUS script, more than 400 design points were evaluated, each with 8 probabilistic steps, leading to over 3200 fin unit cell simulations which required about 24 hours to complete.

Figure 114: Similar to Figure 113 but with Fin ID (= tubing OD) fixed as 0.250".

Keeping the restriction of 0.250" diameter tubing, and lowering the reaction rate to 2X of the current material, the optimum parameters at a refueling time of 60 min are

- fin spacing = $1.4 * 0.2'' = 0.28''$
- fin thickness = $1.0 * 0.004'' = 0.004''$ (minimum considered in study)
- fin OD = $1.33 * 1.5'' = 2.0''$
- fin ID = 0.250" (fixed)

Given the set of results from the analyses for the 4X and 2X reactions, the guidance for heat exchanger design was

- fin spacing between 0.2" and 0.28" or about 4 to 5 fins per inch. Choose 0.2" spacing.
- 0.004" thick fins
- fin OD between 1.6" and 2.0" (area of 2 to 3.1 in² per tube)
- 0.250" tubing to use a standard size & reduce the number of tubes

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For the subscale system, a heat exchanger diameter of 4.5" was selected having a cross sectional area of 15.9 in². With 8 heat exchanger tubes, this gives an area of 1.99 in², consistent with the 4X optimal design.

This design produces a 50% reduction in conduction enhancement weight compared with 4% aluminum foam – $(0.004 \text{ in of Al}) / (0.2 \text{ of HX}) = 0.02$ or 2% dense. This does not account for any additional mass which may be needed for fin spacing or corrugation stiffening. Since the tubing mass scales roughly as the tubing diameter squared, reducing the diameter from 0.375" to 0.250" the mass is decreased by

$$(0.375^2 - 0.250^2) / 0.375^2 = 0.55 \text{ or } 55\%.$$

Increasing the tube number from 24 to 30 is a 25% increase. Thus, the net mass change compared with Prototype 1 for the tubing is a 55% - 25% = 30% improvement. The masses of the conduction enhancement and tubing are roughly the same, so the weighted average decrease in mass for the second generation heat exchanger would be about $(50\% + 30\%) / 2 = 40\%$.

6.2.3 Full Cross Section Modeling

Specific tubing positions were determined using FEA simulations conducted on a larger length scale. For the intermediate size of Prototype 2, a configuration of eight heat exchanger tubes, heat exchanger outside diameter of 4.5 inches and cylindrical vessel straight section length of 16 inches was selected to meet this general target and satisfy the average tubing density of the unit cell heat exchanger optimizations. Details of this configuration are discussed below and shown in Figure 99.

To determine specific positions of the eight heat exchanger tubes, both steady state and transient thermochemical FEA simulations were conducted. For these analyses, models providing heat generation and hydrogen capacity were needed for the specific material to be used. Initially, the anticipated material for the second prototype was attrition milled NaAlH₄ with 3% TiCl₃ * 1/3 AlCl₃. For the transient analyses, the kinetics model was recalibrated to the response of this material. Comparison of the updated model and data is shown in Figure 115 indicating good agreement.

For initial, broader design studies, steady state analyses were used and were reasonable approximations of the thermochemical response for the linear portions of the curves in Figure 115 when initial temperatures are moderately close to the steady state solution. In the steady state simulations, the same material data of Figure 115 were represented more simply with a table of effective capacities (H₂ weight %) versus time and temperature.

With eight tubes and a circular heat exchanger, a high degree of symmetry existed. Variations in the tube positions were conducted by maintaining circumferential symmetry, i.e. each tube was located at a multiple of 45 degrees, but the radial positions were varied independently for two sets of tubes: the four tubes on the vertical and horizontal lines at a radius of r₁ (see Figure 116 (c)) and those on +/- 45 degree lines at r₂. The outside radius of the heat exchanger is denoted by r₀ = 2.25 inches. For the purpose of conducting sensitivity studies, the tubing positions were then specified by the two tubing radii ratios, r₂/r₁, and r₁/r₀. Figure 116 shows the tube positions and temperature contours for three different optimized values of r₂/r₁ and r₁/r₀.

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Figure 115: Absorption data & model for 3% $\text{TiCl}_3 \cdot \frac{1}{3} \text{AlCl}_3$ attrition milled material.

Figure 116: Tube positions and temperature distributions for three tubing configurations (a) $r_2/r_1 = 1.0$ & $r_1/r_0 = 0.6$; (b) $r_2/r_1 = 0.7$ & $r_1/r_0 = 0.72$; (c) $r_2/r_1 = 0.6$ & $r_1/r_0 = 0.8$.

In the prior unit-cell heat exchanger analyses, the fin geometry was modeled explicitly. With the current cross-section model, this is not the case, and effective properties for the fin/hydride mixture must be determined, particularly for the thermal conductivity. This was done by conducting unit-cell simulations with estimates for the effective thermal conductivity to achieve the best match of the hydride temperature cumulative distribution function. The result for the effective thermal conductivity was essentially the same as a linear rule of mixtures, with the deviation being a multiplier of 0.9. In the model, differences between inlet and exit oil temperatures were calculated and prescribed, but amounted to only a few degrees and were not significant. Insulation on the vessel exterior and heat loss through convection to the ambient air were also included. In the steady state analyses, the heat fluxes vary with temperature in a manner consistent with the data of Figure 115 but are constant in time and represent the average over a 30 minute refueling time frame. Thus, these

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initial analyses do not capture details such as temperature spikes but are useful for relative comparisons of one tubing configuration versus another.

The performance metric of the heat exchanger in the steady state analyses was temperature uniformity. To eliminate the influence of the “tails” of the distribution function, the temperature uniformity was measured as the temperature difference between the 5% and 95% temperatures, i.e. the temperature difference over 90% of the hydride volume. Results of over 60 FEA models are given in Figure 117 in which the ΔT results are plotted versus both the $r1$ and $r2$ values of those simulations. Surprisingly, the minimum ΔT (most uniform temperature distribution) is essentially the same for different values of $r2/r1$. More intuitively, all optimal $r1$ and $r2$ pairs essentially straddle the value for $r2/r1 = 1.0$. Note that the plots in Figure 116 are the optimal configurations at the minima in Figure 117, and since they all have essentially the same temperature uniformity, are equally valid candidates for the second prototype.

Figure 117: Temperature differential from steady state analyses for relative comparisons of a variety of tubing configurations.

Transient analyses, which require roughly 100X more time to simulate, were conducted for a number of configurations that were down-selected from the steady state analyses. In these simulations, a hydrogen pressure of 100 bar, oil temperature of 80°C and convection coefficient of 1500 W / m² C were used. Results comparing two configurations which have essentially the same steady state temperature uniformity are shown in Figure 118. It is apparent that the transient responses are remarkably similar, *reinforcing the utility of the steady state analyses*. Other studies indicated that the optimal tube positions using steady state analyses were also the optimal tube positions based on transient analyses. For simplicity of system fabrication, the symmetric design with $r2/r1 = 1.0$ and $r1/r0 = 0.6$ (2.7/4.5) was selected for the second prototype.

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Figure 118: Transient response curves for two different tubing configurations that have nearly identical steady state temperature uniformity (contour plots are from steady state analyses).

Other transient simulations were performed to examine the effect of varying the effective thermal conductivity that could be tied directly to changing the fin spacing. The results for four cases are shown in Figure 119:

- 1) baseline design from unit-cell optimization of fin spacing (fins comprising 4% to 5% of the system mass)
- 2) 2 times the related effective thermal conductivity associated with case 1)
- 3) 0.5 times the baseline conductivity
- 4) 0.1 times the baseline conductivity which is representative of having no fins

Note that the first reaction from NaH to Na_3AlH_6 proceeds rapidly for all cases since the applied pressure of 100 bar is well above the equilibrium pressure for this reaction even as the temperature increases. However, for the Na_3AlH_6 to NaAlH_4 reaction, the refueling time is slowed significantly for the 0.1X case due to heat transfer limitations. For the 0.5X case, by adding fin mass of approximately (5% / 2) or 2.5% of the system mass, the refueling time is greatly reduced. Adding another 2.5% of system mass improves to the 1X curve (from the orange to red line) which in the trade-off between capacity and refueling time, would appear to be a desired improvement. However, adding more fins and increasing system mass by another 5% to achieve a 2X thermal conductivity level only improves refueling time from the red to blue lines, indicating rapidly diminishing returns.

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Figure 119: Influence of thermal conductivity (realized through varying fin spacing) on transient absorption curves.

The model was also applied in a simple study to examine the effects of warm-up transients. Figure 120 shows the transient H₂ absorption curves for different starting temperatures of the system. The same constant oil conditions used previously were also applied in this study. From this, we see there is a 400 to 500 second lag when starting at 20°C.

Figure 120: Transient absorption curves for different initial temperatures.

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6.3 High Level Systems Modeling for Materials Evaluation

The attribute of solid state hydrogen storage materials that is most commonly the focus of evaluations is reversible hydrogen weight percent. Other material characteristics, including density, charging pressure, enthalpy and conductivity can influence the weight of storage system components and hence the overall hydrogen weight percent that is ultimately of interest. However, accounting for these effects involves some level of storage system representation that typically is not undertaken when making material assessments and comparisons.

To communicate system design knowledge to the hydrogen storage community, a simple model that represents the system elements and trade-offs on a high level was developed so that overall system performance can be estimated without the burden of detailed design studies. This work is represented in Publication 3 and Presentation 9. The model should be useful to evaluate novel materials in a more complete manner for a better assessment of their potential when implemented in a storage system. While the model has been derived based on the design of the NaAlH₄ Prototype 2 system, the key attributes are sufficiently general to be applicable to a range of system designs. Using this approach, the properties of materials can be related more precisely to goals for overall system performance with modest additional effort.

Often there is a chasm between the development of novel hydrogen storage materials and the estimation of the overall system performance using these materials. The reasons for this are varied including the different technical nature of the two areas, lack of material data and a wide range of possible system designs. To facilitate such preliminary material evaluations, the model in this section is an initial attempt to develop a method that includes important material properties and yet is generic to the system design and easy to implement. The approach developed draws upon the modeling used in the design of the NaAlH₄ based storage system and includes material/system trade-offs for: 1) pressure and temperature dependence of capacity, 2) hydride density, 3) reaction enthalpy and 4) hydride thermal conductivity.

The model focuses on the gravimetric performance during refueling of an in-situ rechargeable system, since this is the most demanding operation step for producing the pressure and temperature conditions that are desirable from the material's perspective. To simplify model implementation, reaction kinetics will not be tracked in detail over time, but rather will be reduced to the hydrogen weight fraction at a specific time, i.e. the *effective capacity*. The heat transfer equations are based on steady state conduction, which is a reasonable approximation for high capacity materials over most of the absorption reaction. To develop aspects of the model and determine ranges of constant values, the FEA described above for Prototype 2 was applied.

Details of the model are presented in the appendix of Section 11.5.

A number of sensitivity studies were performed examining the effects of 1) the temperature width of the $w(T, P)$ trapezoid in Figure 150; 2) hydride powder density; 3) enthalpy and 4) thermal conductivity. The results of study 1) are shown in the left hand graph of Figure 121. For a refueling time of $t_w = 900$ s, reducing the width of the trapezoid top in Figure 150 left graph from 30 deg. C to 10 deg. C, reduced w_{sys} by 9%. For $t_w = 300$ s, w_{sys} is reduced by 16%. The results of sensitivity study 2) are shown in the right hand graph of Figure 121 which is for $t_w = 900$ s. Doubling the hydride powder density from 0.45 g/cc to 0.9 g/cc increases the overall system weight fraction by 22%. This high sensitivity occurs because increasing the hydride density has a direct reduction of po or vessel volume and mass. For study 3), reducing the reaction enthalpy from 40 kJ/mole to 20 kJ/mole increased w_{sys} by 8% for $t_w = 900$ s, and by 21% for $t_w = 300$ s.

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Finally, increasing the thermal conductivity from 0.5 to 1.0 W/m C increased w_{sys} only 0.7% and 1.6% for 900 s and 300 s respectively. If the heat exchanger conduction enhancement exists on a fine length scale, the distance over which conduction must occur through the hydride powder is also small, reducing the significance of hydride conductivity. Since the current model neglects some effects that are less material properties oriented and more systems oriented, the approach is somewhat optimistic so that the above results should be taken as first order estimates of material property significance rather than fully accurate results.

Figure 121: Left – results from varying temperature width of capacity. Right – effect of hydride density.

6.4 Fabrication of Prototype Components and Assemblies

The second prototype system was shown as a three dimensional solid model in Figure 99, and for thermocouple instrumentation, also had a boss at the far end of the vessel. The system was fabricated with the following major steps:

- Form the heat exchanger fins and tubing
- Assemble the heat exchanger
- Fabricate the vessel lining in two pieces
- Weld the tubing to the integrated manifold section of the liner (see Figure 101).
- Insert the heat exchanger into the second liner section and weld the two liner pieces
- Wind the assembled liner with carbon fiber composite and proof test with dry gas
- Install the vessel onto the shaker rig within the assembly glove box
- Load the catalyzed NaAlH₄ (3525 g)
- Install the combined porous metal filter / cap

To push for weight minimization, thin 0.004” aluminum fins were used for the heat exchanger. However, initial testing indicated that loads during hydride packing could cause the fins to deform significantly. To strengthen the fins, reinforcing features were formed which eliminated the deformation. For the prototype 2 fins, a number of reinforcement patterns were examined with FEA

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considering practical limits in formability. The pattern shown in Figure 122 and Figure 123 was selected as the best. Initial fins were fabricated from half-hard 3003 aluminum by the Lyons Tool and Die Company. However, the resin curing cycle of the composite vessel would expose the fins to temperatures which would anneal and soften the fins to unacceptable levels. To address this, fins were formed from 6061-O aluminum and subsequently precipitation hardened through heat treatment to the 6061-T6 condition.

Figure 122: (a) fin stack showing reinforcing features; (b) example displacement contour plot from FEA to select best reinforcement design.

Figure 123: Heat exchanger fin geometry; (a) fabricated fin with reinforcement features; (b) red circles indicate the cross section locations of the four thermocouples.

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The contoured tubing was secured in a positioning jig, a set of 80 fins was installed on the tubing and the U shaped tubing ends were welded in place as shown in Figure 124 (a). Next, the aluminum fins were carefully positioned along the tubing as shown in Figure 124 (b) using 3/16" (0.1875") bar stock to set the spacing at $0.1875 + 0.004$ " (fin thickness) = 0.1915" or just under the nominal design spacing of 0.200". High temperature, low viscosity epoxy with a use temperature up to 265°C was applied to mechanically and thermally couple each of the more than 640 fin collars to the heat exchanger tubing with an added weight of less than 10 g. After curing the epoxy, four 0.032" diameter, sheathed type K thermocouples were inserted into preformed holes in the fins to a layer located ¼ of the way along the heat exchanger length. These thermocouples were positioned in the fin cross section as given in Figure 123 (b).

Figure 124: (a) Prototype 2 heat exchanger assembly with consolidated fin stack; (b) assembly with distributed fins.

Aluminum foam was used to provide conduction enhancement in the two domed end sections where the use of fins was impractical. After assembly of the aluminum foam, heat exchanger and main liner section, the machined liner dome / oil manifold was electron beam welded to the tubing and the two liner sections were welded together as shown in Figure 125 (a).

Spencer Composites Corporation then wound the liner assembly with carbon fiber / high temperature epoxy per the previously designed winding pattern - Figure 125 (b). After curing the epoxy, the system was pressure tested to 1.5 times the working pressure of 1500 psi or to 2250 psi. Normally water is used for such "hydro" testing of pressure vessels, but in this case, dry gas was used to prevent water from potentially being driven into small gaps and voids within the interior assembly that would be difficult to remove through subsequent evacuation and/or heating. Four strain gauges, two in the hoop direction and two in the axial direction, were installed at the midpoint of the length at 90 degree intervals. After application of the composite overwrap, the oil supply and return tubing as well as oil manifold lid were welded in place.

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Figure 125: (a) completed heat exchanger / liner assembly; (b) addition of carbon fiber wound composite.

6.5 Powder Loading

A large 5' x 5' x 4' acrylic glove box, pictured in Figure 126, was used to maintain an inert environment while the system was loaded with hydride material. A high nitrogen flow rate of 40 liters / minute was developed for dilution after the box was initially sealed and then a lower flow rate system up to 6 liters / minute was used to control purging during operation.

To minimize stresses on the prototype vessel as well as the roller elements during vibration, a support structure was designed as shown in Figure 127. The structure was also designed to minimize the additional weight which the shakers will need to move, since the rating of the shakers is estimated to be just adequate for the 15 to 20 lbs. of the vessel, hydride and supports.

Figure 126: 5' x 5' x 4' glove box used for Prototype 2 powder loading.

To minimize stresses on the prototype vessel as well as on the roller elements during vibratory powder loading, a support structure was designed as shown in Figure 127. The structure was also designed to minimize the additional weight which the shakers would need to move, since the rating of the shakers was estimated to be just adequate for the 15 to 20 lbs. of the vessel, hydride and supports.

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The apparatus was constructed and operation procedures were developed for controlling the new shakers and amplifiers using electronic function generators. Glove box gas purity was measured with an oxygen analyzer to be between 2 and 3 ppm before introducing any NaAlH_4 and to be below the detectable limit of 10 ppb after opening a sacrificial tray of NaAlH_4 .

Figure 127: Solid model of shaker assembly with linear roller bearings and vessel support for independent biaxial vibration.

The powder loading of the second prototype was conducted at a rate of between 100 and 200 g / hr due to the manual nature of operating valves and buttons to dose the powder and vibrate the system. The speed and economic viability of such a loading process could be improved dramatically with automated operation and process optimization to minimize vibration times. After loading the entire vessel, a core of powder was removed from the centerline to allow insertion of a porous stainless steel filter which had been welded to the vessel cap. Powder residue was cleaned up inside the assembly glove box, the access door was removed and the system was dismantled from the shaker frame. The system was then weighed and compared with the empty weight to determine that 3525 g of hydride had been loaded into the system. This was within 10 g of an estimate based on accounting of powder during the loading process.

6.6 Testing Hardware Development & Initial Data

UTRC's custom "50 Gram" Sievert's apparatus previously discussed in Section 3.4.1 was enhanced primarily with the addition of a secondary pressure vessel designed specifically for containment of the prototype in case of vessel failure or leakage. Sketches of the vessel configuration are shown in Figure 128 and the actual hardware in Figure 129. With this design, all connections and lid pass-throughs could be made easily. The lid / system assembly was lowered using a chain-fall and lockable guides were present on each side of the lid for additional support and safety. A positive displacement gear pump was added to achieve the moderately high pressures (65 psi) needed to circulate the oil rapidly within the prototype heat exchanger tubing. An oil heating/cooling thermal control system was also developed which was sealed from air to prevent degradation of the Paratherm MR oil.

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Figure 128: Testing apparatus secondary containment design.

Figure 129: Secondary containment construction and assembly.

A preliminary desorption test was performed at 150°C with final desorption pressures of nominally 15 psi. An absorption test was then conducted with peak hydrogen pressures of 1500 psi. Because of the size of the accumulator volume relative to the system capacity, the hydrogen was supplied to the system in doses after which the pressure would drop as hydrogen was absorbed, reducing the absorption kinetics. The hydrogen mass supplied to the system versus time is plotted in Figure 130. After 3 hours, 136 g of hydrogen had been stored within the system with an estimated 13 g of that being in the state of compressed gas. Temperature data are plotted in Figure 131. After an initial warm up period, the system is pressurized in doses with nominally 100 bar hydrogen. The waviness occurs due to the hydrogen dosing and pressure fluctuations. For about 45 minutes, the exothermic absorption reaction produces a clear increase in hydride/fin temperature above the circulated oil temperature, after which the interior temperatures are seen to lag during fluctuations of the oil temperature due to thermal inertia (heat capacity).

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Figure 130: Absorption data for the first experiment performed at pressures starting at 1500 psi and dropping due to absorption in between each data point dosing.

Figure 131: Temperatures for the four internal thermocouples and heat transfer oil during a Prototype 2 absorption test.

Before pursuing subsequent tests, improvements were made to the testing apparatus including the addition of a Coriolis force flow meter similar to the type used in Prototype 1 testing, but of smaller size. During a system pressurization to check the operation of the flow meter, a leak developed in the system. This was traced to the vessel itself as shown in Figure 132. It is likely that the failure

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occurred at the juncture of the longitudinal and circumferential liner welds where a slight distortion of the cylindrical liner section and lack of alignment of the two liner pieces was noted. While it would be possible to continue testing by upgrading the secondary containment vessel to 1500 psi and pressurizing this outer vessel to the same level as the prototype system, the required resources would be prohibitive at the late stage in the contract while the additional knowledge to be gained would be marginal.

Figure 132: Soap bubble indication of gas leak locations.

6.7 Component Weights and Volumes

The listings of component weights and volumes are given in Table 12 and Table 13.

- Converting from pounds to grams, 15.32 lbs. = 6846 g.
- Converting the energy in 1 kg H₂ to Wh, the lower heating value of H₂ is 120 MJ / kg H₂; a Wh = 1 J/s * 3600 s = 3600 J; or 120e6 J / kg H₂ * 1 Wh / 3600 J = 33,333 Wh / kg H₂

With a measured capacity of 136 g, the system metrics are

- Gravimetric capacity = 136 g H₂ / 6846 g System = 0.020 g H₂ / g System = 2 wt%
- Volumetric capacity = 136 g H₂ / 6450 cc System = 0.021 g H₂ / cc System = 0.021 kg H₂ / L
- Volumetric capacity = 0.021 kg H₂ / L * 33,333 Wh / kg H₂ = 700 Wh / L
- Average powder density = 3525 g CCH / 4900 cc CCH = 0.72 g CCH / cc CCH

These are the values reported in Table 2 for Prototype 2.

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Table 12: Prototype 2 component weights in units of pounds.

Internal Parts:	Quantity	Part	Part Weight, [lbs]	Total Weight, [lbs]
	8	Tube	0.131	1.05
	2	End Plate	0.076	0.152
	2	Oil Tube	0.021	0.042
	1	U-Bends Total	0.068	0.068
	16	Spacers	0.0043	0.068
	84	Fins	0.0060	0.51
	8	Fins supports	0.0069	0.055
	1	Filter	0.153	0.153
	1	Aluminum foam pieces	0.191	0.191
	1	Gas Feed & Cap	0.380	0.380
	4	Thermocouples	0.011	0.044
				2.66
Pressure Vessel:	1	Fiber Wrap	1.13	1.13
	1	Liner/Manifold	2.96	2.96
	1	Oil Cover	0.07	0.07
	1	Main valve	0.35	0.35
	1	Pressure tap valve	0.17	0.17
				4.67
Other:		TC fitting, strain gauge wire, ...		0.21
Empty System:				7.55
Powder:	Volume, [in^3]	Hydride Location	Est. Density (lb/in^3)	TOTAL
	247	HX Fins	0.027	6.68
	19	Top End	0.021	0.40
	15	Bottom End	0.022	0.33
	18	Gaps	0.021	0.37
				7.77
			Filled Vessel	15.32
		Gravimetric Efficiency	0.51	

Table 13: Prototype 2 component volumes.

Heat Exchanger	241	cc
Hydride Powder	4900	cc
Filter & Other Internals	73	cc
Vessel Wall	454	cc
Manifold & Externals	782	cc
System total	6450	cc

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Pie charts for the component weights and volumes are given in Figure 133 and Figure 134. From this we see the system gravimetric efficiency is just over 50% with a large portion of the non-hydride mass being from the pressure vessel as expected. The volumetric efficiency is over 70% when accounting for an envelope around the manifold supply lines, but otherwise not including empty regions around the system.

Figure 133: Component mass fractions for the system with a total mass of 6846 grams.

Figure 134: Component volume fractions for the system with a total volume of approximately 6450 cubic centimeters.

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Energy density for the system can also be obtained from the product of the three quantities:

- Hydride powder density
- H₂ weight % capacity
- System volumetric efficiency

Figure 135 shows the system volumetric capacity for various storage material capacities and powder densities. A significant improvement was made from Prototype 1 to Prototype 2, but there remains approximately a factor of 2 difference with the DOE 2007 target.

Figure 135: Sensitivity of volumetric capacity to material capacity and powder density.

6.8 Prototype 2 Absorption Simulation

As a first step to set up simulation of the second prototype, the reaction kinetics model was refit to data obtained in the Sievert's apparatus for the 2% TiCl₃*1/3AlCl₃ + 0.5% FeCl₃ material of Prototype 2. Conditions of the kinetics tests were pressures of nominally 75 and 105 bar and temperatures ranging from 60°C to 180°C. During the testing, the pressures varied by less than 10 bar, with the nominal values given being the average. The data along with the model comparison are plotted in Figure 136 and Figure 137.

During the current model parameter determination procedure, the van't Hoff line slope (enthalpy) and intercept (entropy) were adjusted. This was done to produce the reductions in reaction rates occurring at higher temperatures that are driven by an increase in the equilibrium pressure which approaches the applied charging pressure. By doing this, all temperature dependencies for the saturation composition levels (see Equation 7 in Section 11.1.3) were able to be eliminated. Note that data at (75 bar, 100°C), (105 bar, 140°C) and (105 bar, 160°C) have sigmoidal shape. In order to fit the

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model to the full range of conditions, the resulting model over-predicts reaction rates for these sigmoidal regions.

Figure 136: Absorption kinetics data for Prototype 2 material at 75 bar. Dashed lines are for the model.

Figure 137: Absorption kinetics data for Prototype 2 material at 105 bar. Dashed lines are for the model.

The new model parameters, which were determined using Matlab, were then incorporated into the ABAQUS model and verified with isothermal simulations for a simple cube geometry, confirming proper implementation.

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A solid model was constructed to represent a cross-section of the second prototype that included tubing walls, filter wall, composite vessel wall, insulation, and most importantly the hydride / aluminum fin region shown in Figure 138. In Section 6.2.3, an effective thermal conductivity for the homogenized fin / hydride “material” had been estimated iteratively from the unit cell model. In this way, an effective thermal conductivity of 4.3 W / m C was determined. With the cross section model, the through thickness temperature distribution (vertical in Figure 104) is not captured, but this is secondary to the radial distribution (horizontal in Figure 104).

Figure 138: ABAQUS cross section model – (a) solid model with thermocouple positions; (b) finite element model; (c) representative temperature contour at the time of peak temperature.

Simulation of the initial heat-up period, during which warm oil is circulated through the system, provided an opportunity to verify and fine tune the thermal parameters. Results from the first simulation using the calculated / estimated values of

- Effective hydride/fin thermal conductivity = 4.3 W / m C
- Convective heat transfer coefficient for oil = $1500 \text{ W / m}^2 \text{ C}$
- Convective heat transfer coefficient for heat loss to air = $5 \text{ W / m}^2 \text{ C}$

are given in Figure 139. The comparison is moderately good, but after a few trials, it was discovered that modifying one parameter:

- Effective hydride/fin thermal conductivity = 6.0 W / m C

produced the comparison in Figure 140, which gives quite close agreement. Reduced thermal contact resistance due to the high degree of packing could be the reason for the higher effective conductivity.

Note that the thermocouples are sheathed 0.032” diameter, and were routed axially or perpendicular to the cross section plane to minimize the influence on the temperature field. Re-examining Figure 104, the thermocouples would have a diameter approximately equal to the horizontal dimension of the blue rectangle for the tubing wall, so some influence on or averaging of the temperature field will occur, but the predominant thermal behavior can be captured reasonably consistently for the four different thermocouples as shown in Figure 140.

Prototype 2 System Studies

Figure 139: Model comparison for warm-up period with preliminary parameters. Dashed lines are for the model.

Figure 140: Comparison for warm-up period with modified thermal conductivity. Dashed lines are for the model.

Prototype 2 System Studies

Examining the simulation comparison which includes hydrogen pressurization, we see from Figure 141 that the model predicts the reaction will occur faster than the experiment both for higher peak temperature and for more rapid hydrogen flow rate. Possible causes for this discrepancy are

1. Inaccuracy of the kinetics model – recall the model over-predicted the reaction rate for some conditions, particularly where there was sigmoidal shape.
2. Restriction of hydrogen mass flow so that the local hydrogen pressures at various points within the system are below the measured inlet pressure.
3. Contamination of the hydride such that the reaction rate is slowed by roughly a factor of 2 but the ultimate capacity is nearly the same.

Cause 1 was investigated briefly by refitting the kinetics model to more closely follow the primary conditions of 100°C to 140°C at 100 bar. The comparison was not improved significantly. Cause 3 is somewhat unlikely to result in only the kinetics and not the capacity being affected by contamination. Cause 2 is plausible, since the powder densification was aggressive and successful during the fabrication of Prototype 2. Prior efforts with lower density powders and slower material kinetics had not indicated mass transfer issues, especially considering the charging pressure was 100 bar, much higher than conventional metal hydride systems. Therefore, mass transfer was not sufficiently significant throughout most of the project to include in the simulation approach. However, with the improvements in system powder packing and also reaction kinetics, it seems that this phenomenon should now be included in simulations as well as system design.

Figure 141: Comparison of (a) temperatures and (b) hydrogen mass flow for the exothermic hydrogen absorption. Dashed lines are for the model.

By introducing reaction rate reduction factors of nominally 0.5 for both the r_2 and r_4 reactions (see Table 15 in Section 11.1.1), the comparisons of Figure 142 are now reasonable for both temperatures and mass flow, which also indicates consistency between the enthalpy, heat capacity and heat transfer.

Prototype 2 System Studies

Figure 142: Comparison of (a) temperatures and (b) hydrogen mass flow for a simulation having reaction rate reduction factors of 0.5. Dashed lines are for the model.

Alternately, a pressure reduction factor of 0.65 was multiplied on the time dependent hydrogen pressure history producing the results in Figure 143. Note this still produces a spatially uniform pressure field, whereas if mass transfer was restricted, there would be pressure gradients that would be predominantly radial.

Figure 143: Comparison of (a) temperatures and (b) hydrogen mass flow for a simulation having a pressure reduction factor of 0.65. Dashed lines are for the model.

Conclusions

7 Conclusions

7.1 Summary

The current contract has examined a wide range of materials and systems technologies in the development of two NaAlH_4 based hydrogen storage prototypes. A number of technical areas which are not issues for conventional metal hydride systems were identified and addressed including requirements for higher pressure, incorporation of composite vessels, use of non-reactive heat transfer oil, inert glove box fabrication and enhanced powder loading techniques. A combination of materials development, small scale engineering experiments, detailed modeling, high level modeling, prototype fabrication and system testing contributed to establishing a strong basis for estimating the realistic performance of NaAlH_4 class storage systems as detailed below.

The Prototype 2 gravimetric and volumetric performance elements are given as follows:

- Hydride mass = 3525 g
- System mass = 6948 g
- Adjusted system mass = 6846 g after removing:
 - Optional pressure tap valve
 - Three additional thermocouples
 - Strain gauge leads
- Hydride volume:
 - 4610 cc if confined to designed region
 - 4900 cc if extended to include gaps
- System envelope volume $\approx$ 6450 cc
- Stored hydrogen from absorption test = 136 g

Potential improved performance can be projected based on the following:

- An average loaded hydride density of 0.85 g/cc. This density was obtained consistently in powder column densification tests on NaAlH_4 associated with Table 10. As mentioned in Section 5.1, because of the loss of attrition milling capability, this milling sequence could not be employed in the actual prototype. Results from a number of experiments have demonstrated that a finned tube heat exchanger can be loaded to essentially the same density as measured in powder column tests, i.e. 0.85 g/cc. If we also make minor improvements to the system design, the loaded hydride mass would be $0.85 \text{ g/cc} \times 4900 \text{ cc} = 4165 \text{ g}$ for the current scale prototype.
- If we scale the vessel to nominally full size which would be approximately 10 times larger than the current prototype (1.36 kg per vessel – four vessels integrated into an automobile), there will be reduction in specific mass (mass per unit volume) which will be most significant for two components:
 - The liner is needed for its gas impermeability, chemical inertness and as a form for filament winding. The 10X vessel can retain the 0.020" liner thickness which would result in the liner mass scaling as $(\text{Volume})^{2/3}$ or by a factor of $10^{2/3} = 4.64$. With the prototype pressure vessel, the liner is over 70% of the mass, weighing 1375 g compared with 515 g for the composite overwrap.
 - The conventional hydrogen valve is quite heavy, was not optimized for weight and could accommodate the 10X flow rates. As a first approximation use the same mass for the 10X system.

Conclusions

- The above two adjustments result in a gravimetric efficiency of 0.63 (kg hydride / kg system)
- At 0.85 g/cc, 140 C and 100 bar, the compressed gas storage is effectively 0.25% (kg H₂ gas / kg hydride).
- To meet a **2.3 wt% system performance**, the total effective wt% of the material would need to be

$$2.3\% / 0.63 = 3.65\%$$
- Accounting for the compressed gas, the capacity of the material then would need to be

$$3.65\% - 0.25\% = 3.40\%$$

This capacity is borderline achievable with NaAlH₄, but refueling times and desorption temperatures would still be in the neighborhood of 30 minutes and 150°C, higher than what is targeted.

A summary of the performance metrics for the current and projected prototypes is repeated from Figure 1 in Figure 144. The additional projections have been made on a high level, i.e. without specific methods as to *how* these would be achieved, where a balance has been sought for the challenges for the material versus the system. From this, to meet the DOE 2007 target, a 6.5 wt% material would be needed with a packed powder density of 0.8 g/cc and system gravimetric efficiency of 0.67. The 2010 target requires an 8.0 wt% material, 0.850 g/cc packing and system gravimetric efficiency of 0.75.

Complex Compound Hydride Storage System (CCHSS) Performance Metrics

Material & Version:		NaAlH ₄ Prototype 2	NaAlH ₄ Projected	TBD hydride	TBD hydride	DOE Targets	
Characteristics & Metrics	Units					2007	2010
Material gravimetric capacity	% kg H ₂ / kg hydride	3.4%	3.4%	6.5%	8.0%		
H ₂ charging pressure	bar	100	100	70	50		
Packed powder density	kg hydride / m ³ powder	720	850	800	850		
Material volumetric capacity	kg H ₂ / m ³ powder	24	29	52	68		
System gravimetric efficiency	kg hydride / kg system	0.515	0.63	0.67	0.75		
System volumetric efficiency	m ³ powder / m ³ system	0.76	0.76	0.7	0.7		
Normalized compressed gas	% kg H ₂ gas / kg hydride	0.5%	0.3%	0.3%	0.2%		
System gravimetric capacity	% kg H ₂ / kg system	2.0%	2.3%	4.5%	6.1%	4.5%	6.0%
System gravimetric capacity	kWh / kg	0.66	0.8	1.5	2.0	1.5	2.0
System volumetric capacity	kg H ₂ /m ³	21.1	24.0	37.8	48.6	36	45
System volumetric capacity	kWh/L	0.70	0.80	1.26	1.62	1.2	1.5

Notes

a: Improved catalysts & processing

b: Demonstrated powder packing enhancement

c: Improved densification & size scaling

d: Materials discovery

e: Reduction of charging pressure & vessel mass

Figure 144: System performance metrics status and projections.

In addition, the following capabilities were developed over the course of this project which could have future applications in other hydrogen storage activities:

- An atomistic simulation framework to study detailed aspects of real and virtual compounds and reactions.
- Transient thermochemical finite element analysis with a versatile reaction kinetics model.
- High level models for heat exchanger optimization and sensitivity to material properties.
- Powder densification methods to serve as a repeatable, well quantified approach to evaluate new material powder densities and thus the material volumetrics.
- Facilities to fabricate and safely test reactive hydrogen storage prototypes of the 1 kg H₂ scale

Conclusions

7.2 Recommendations

Lessons learned throughout the execution of this contract include:

- Key systems technologies associated with applying NaAlH_4 and similar materials are the use of lightweight carbon fiber vessels and advanced methods of powder loading.
- Powder densification is as significant as hydrogen weight percent for volumetric performance.
- As prepared, NaAlH_4 is reactive with water and air. For other CCH material candidates, on-board recharging will require rapid kinetics with hydrogen which is likely to lead to reactivity with water and air that is similar to that of NaAlH_4 . To address this, mitigation methods would be beneficial to inhibit exposure to water and limit the rates of undesired reactions.
- For NaAlH_4 , high purity hydrogen is required to maintain capacity during cycling.
- Finned tube heat exchangers are superior to those using metal foam due to more efficient long range heat transport.
- A gravimetric efficiency of 50% and volumetric efficiency of 70% for this class of system are realistic and achievable.
- It is beneficial to conduct modeling for system design at a number of complexity levels:
 - Detailed models (spatial resolution, transient effects, ...) when needed and to justify simplifying assumptions.
 - High level models to facilitate inclusion of a wider scope of optimization trade-off dependencies and for consistency checks.
- The approach of designing and fabricating at least two prototype versions is beneficial, particularly when including new or unconventional components and processes.
- Significant resources can be required in prototype development for:
 - Material production and processing
 - Supporting fabrication hardware
 - Safe testing hardware.
- A $(1/2)^3 = 1/8$ scale (1/8 kg H_2) system is a good balance for reasonable hardware investment and ability to conduct projections to full scale.

The high level recommendations for future research directions are

- Greater powder densification along with engineered hydrogen mass distribution that are compatible with overall system fabrication procedures.
- Continued heat exchanger enhancement such as size scale reduction for fluid flow channels which is sufficiently lightweight and application of higher performance yet chemically inert heat transfer liquids.
- Vessel liners which are lighter-weight than stainless steel and can withstand elevated temperatures as well as hydride chemical exposure.

Publications and Presentations

8 Publications and Presentations

Publications

1. D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine and D. Dedrick, "Fundamental Safety Testing and Analysis of Hydrogen Storage Materials and Systems," submitted for publication in the Proceedings of the 2nd International Conference on Hydrogen Safety, San Sebastian, Spain, September 2007.
2. M. Cao, S. Arsenault, and D. Mosher, "Preliminary Study on Nanometer-scale Gamma-aluminum Powder Densification Through Vibration," Proceedings of IMECE2006, 2006 ASME International Mechanical Engineering Congress and Exposition, November 5-10, 2006, Chicago, Illinois, USA.
3. Daniel A. Mosher and Donald L. Anton: "Beyond Weight Percent - The Influence of Material Characteristics on Hydrogen Storage System Performance," in *Materials and Technology for Hydrogen Storage and Generation*, edited by G-A. Nazri, C. Ping, R.C. Young, M. Nazri, and J. Wang (Mater. Res. Soc. Symp. Proc. 884E, Warrendale, PA, 2005), GG4.3.
4. Xia Tang, Daniel A. Mosher and Donald L. Anton: "Practical Sorption Kinetics of TiCl₃ Catalyzed NaAlH₄," in *Materials and Technology for Hydrogen Storage and Generation*, edited by G-A. Nazri, C. Ping, R.C. Young, M. Nazri, and J. Wang (Mater. Res. Soc. Symp. Proc. 884E, Warrendale, PA, 2005), GG4.4.
5. C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," to be submitted to Phys. Rev. B.
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9. S. M. Opalka and D. L. Anton, "First Principles Study of Sodium-Aluminum-Hydrogen Phases," J. of Alloys and Compounds 356-357 486-489 (2003).

Publications and Presentations

Presentations

1. D. Mosher, S. Opalka, X. Tang, S. Arsenault and B. Laube, "Development and Application of New High Capacity Hydrogen Storage Materials," IEA Task 22 Meeting, Monterey, California, January 29, 2007.
2. D. Mosher, S. Arsenault, X. Tang and D. Anton, "Design, Fabrication and Testing of NaAlH₄ Based Hydrogen Storage Systems," MH2006 International Symposium on Metal-Hydrogen Systems, Lahaina, Maui, Hawaii, U.S.A., October 1-6 2006.
3. D. Mosher, "Complex Hydride Materials, Systems and Safety," IEA Task 17 / IPHE Joint Meeting, Windermere, UK, May 1-4, 2006.
4. D. Mosher, X. Tang and S. Arsenault, "Material Processing and Densification for Complex Hydride Based Storage Systems," MRS Spring Meeting, San Francisco, CA, April 17-21, 2006.
5. D. Anton, D. Mosher, F. Lynch and J. Senecal, "Risk Assessment of High Capacity Solid State Hydrides," TMS Annual Meeting, San Antonio, TX, March 13-16, 2006.
6. D. Mosher and S. Opalka, "Hydrogen Storage System Demonstration for a Fuel Cell Vehicle Base on NaAlH₄" IEA HIA Task 17 Workshop, Tateyama, Japan, October 23-27, 2005.
7. X. Tang, D. L. Anton, and D. A. Mosher, "Development of NaAlH₄ as an In-Situ Reversible Hydrogen Storage Media" TMS MS&T Meeting, Pittsburgh, PA, September 25-28, 2005.
8. D. L. Anton and D. A. Mosher, "Solid State Hydrogen Storage System Development," Poster presented at the International Partnership for the Hydrogen Economy (IPHE) International Conference on Hydrogen Storage, Lucca, Italy, June 20-22, 2005.
9. D. A. Mosher and D. L. Anton, "Beyond Weight Percent – The Influence of Material Characteristics on Hydrogen Storage System Performance," Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
10. X. Tang, D. L. Anton and D. A. Mosher, "Practical Sorption Kinetics of Several NaAlH₄ Compositions," Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
11. C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic Modeling of Sodium Aluminates," Materials Science & Technology 2005 to be held in Pittsburgh, PA, September 25-28, 2005.
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14. Posters presented at the Hydrogen-Metal Systems Gordon Research Conference, Waterville, ME, July 13-18, 2003.
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14. X. Tang, D. A. Mosher and D. L. Anton, Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
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Abbreviations

10 Abbreviations

Table 14 gives most abbreviations which occur throughout the report.

Table 14: Description of abbreviations.

<i>Abbreviation</i>	<i>Meaning</i>
APS	Air Processing System
ASME	American Society of Mechanical Engineers
CCH	Complex Compound Hydride
DOE	Department Of Energy
FC	Fuel Cell
FPS	Fuel Processing System
HAZMAT	Hazardous Material
HCI	Hydrogen Components, Incorporated
HX, HEX	Heat EXchanger
ksi	Unit of pressure: <u>kilo psi</u> or 1000 pounds per square inch
JBTS	Jet Burner Test Stand
MEC	Minimum Explosive Concentration
MIE	Minimum Ignition Energy
ml	milliliter
MTU	Michigan Technological University
PEM	Polymer Electrolyte Membrane
ppm	parts per million
PS	Proprietary Synthesis
psi	pounds per square inch
SLPM	Standard Liters Per Minute
SM	SPEX Mill
SNL	Sandia National Laboratories
SRNL	Savannah River National Laboratory
TC	ThermoCouple
TM	Tumble Mill
TMS	Thermal Management System
UN	United Nations
US DOT	United States Department of Transportation
UTRC	United Technologies Research Center
wt%	weight percent
XRD	X-Ray Diffraction

Appendices

11 Appendices

11.1 Reaction Kinetics Model

11.1.1 Reaction Descriptions and Definitions

The absorption and desorption of hydrogen to and from the NaAlH₄ based material is characterized by the reversible chemical reactions:

The directions of these reactions are determined by the applied hydrogen pressure compared with the equilibrium hydrogen pressure for each reaction. When the applied pressure is greater than the equilibrium, the reactions proceed to the left, and when the pressure is lower, they proceed to the right. The equilibrium pressure for each reaction is temperature dependent and follows the van't Hoff equation,

$$\ln(P_e) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} = \frac{A}{T} + B$$

When plotting the natural log of the equilibrium pressure (determined from PCI testing) versus the inverse of temperature, the slope then is $\Delta H / R$ and the intercept is $\Delta S / R$. The enthalpy, ΔH , is the amount of heat per mole of H₂ which needs to be exchanged to drive the reactions. When proceeding in the hydriding direction, the reaction is exothermic and when dehydriding, it is endothermic. Based on experiments and analysis in Ref. 1 and Ref. 3,

$$\Delta H_a = 47 \text{ kJ/mol of H}_2$$

$$\Delta H_b = 37 \text{ kJ/mol of H}_2$$

The enthalpies dictate the amount of heat which must be transferred to exchange hydrogen, but they say nothing about the rate at which the reactions will occur. In order to capture this effect for the purpose of system design, it is necessary to model the reaction kinetics. The kinetics of NaAlH₄ have been improved, but are still slow enough that this is the primary rate limiting aspect.

The present modeling approach tracks the reactions with three state variables that represent the weight fractions of the three compositions C₁, C₂, C₃:

The values of the three C_j range between 0 and 1 with the sum of all three being exactly 1. The reaction kinetics are modeled by the rate equations for dC_i/dt presented below. Note that for the two reversible reactions:

Alternately, the notation of r_i will be used to give a separate index number for each *directional* reaction as shown in Table 15.

Appendices

Table 15: Descriptions of the four directional reactions for NaAlH₄.

Label	Action	Reactant	Product
r ₁ or R _{a,d}	dehydriding of Na ₃ AlH ₆	C ₂	C ₁
r ₂ or R _{a,h}	hydriding of NaH	C ₁	C ₂
r ₃ or R _{b,d}	dehydriding of NaAlH ₄	C ₃	C ₂
r ₄ or R _{b,h}	hydriding of Na ₃ AlH ₆	C ₂	C ₃

Based on the applied pressure in comparison with the two equilibrium pressures, different directional reactions will be active as diagrammed in Figure 145.

Figure 145: Activity regime of each directional reaction.

For comparison with experimental data on hydrogen absorbed or desorbed, the related weight fraction of hydrogen is calculated from

$$w = \sum_{j=1}^3 w_j C_j = w_2 C_2 + w_3 C_3 = 0.0187 * C_2 + 0.056 * C_3$$

In actual experiments, the full 5.6 wt% is not realized, due to the addition of catalyst mass, inert or unreactive constituents and possibly incomplete reactions. As an example, if the reaction saturates at 4 wt%, then calculate $v = 4/5.6 = 0.714$ and take

Equation 5
$$w = \sum_{j=1}^3 v w_j C_j = v * (w_2 C_2 + w_3 C_3) = 0.714 * (0.0187 * C_2 + v * 0.056 * C_3)$$

What ultimately is needed for implementation in a simulation code such as ABAQUS is the heat source/sink, q which has units of energy / (time volume). Since the hydriding reaction direction results in energy being released, a positive heat generation flux will occur when a hydriding product is increasing, i.e.

$$q = \left(\frac{dC_2}{dt} \right)_{r_1 \text{ or } r_2} * \Delta \tilde{H}_a * \rho + \left(\frac{dC_3}{dt} \right)_{r_3 \text{ or } r_4} * \Delta \tilde{H}_b * \rho$$

The powder density is modeled as being constant, with typical ranges between 500 and 800 kg/m³.

Appendices

11.1.2 Reaction Rate Equations – Version 1

A number of different functional forms were obtained in the literature to model the reaction kinetics. These are listed in Table 16. Note different symbols have been used in these equations, but that most of them have a common structure which divides the dependence on temperature, pressure and composition into the factors

$$\left(\frac{dC_j}{dt} \right)_{r_i} = f_T(T) * f_P(P) * f_C(C_k)$$

where the indices have the following meaning:

- i for reaction r_i
- j for composition product C_j
- k for composition reactant C_k

The temperature dependence factor will be given an Arrhenius form for the mobility effect,

$$f_T = D_i \exp\left(-\frac{E_i}{RT}\right)$$

For the hydriding direction, one could chose to have the rate proportional to $(P - P_e)$ or $(P - P_e)/P_e$ or $\ln(P/P_e)$, all of which are zero when $P = P_e$. Note that $(P/P_e)^a$ is not zero when $P = P_e$. Without specific information to distinguish which form is better, the following was chosen. For hydriding,

$$f_P = \left(\frac{P - P_{e,i}}{P_{e,i}} \right)$$

Since the convention used in assigning values to i is such that the even values are hydriding reactions, we can multiply by -1^i to have it be valid for both hydriding and dehydriding:

$$f_P = (-1)^i * \left(\frac{P - P_{e,i}}{P_{e,i}} \right)$$

The dependence on composition will be chosen to be a simple power law on reactant concentration:

$$f_C = (C_k)^{\chi_i}$$

Combining the model factors:

Equation 6

$$\left(\frac{dC_j}{dt} \right)_{r_i} = D_i \exp\left(-\frac{E_i}{RT}\right) * \left(\frac{P_{e,i} - P}{P_{e,i}} \right) * (C_k)^{\chi_i}$$

Appendices

Table 16: Functional forms for reaction kinetics.

Source	Equation	Applicability
Ref. 4	$-\frac{d[A]}{dt} = K[A]^a[B]^b \dots$	Homogeneous reactions: $aA + bB + \dots \rightarrow cC + dD$
Ref. 5	$\frac{dC}{dt} \propto K(T) \frac{P_e - P}{P_e} C_0$ $K(T) = B \exp\left(-\frac{E}{RT}\right)$	Metal hydrides
Ref. 6	$\frac{dC}{dt} = f_T f_P f_H$ $f_T = A_1 \exp\left(-\frac{A_2}{T}\right)$ $f_P = \frac{P_e - P}{P_e}$ $f_H = \frac{(\zeta - \zeta_F)}{(\zeta_l - \zeta_F)}, \text{ is hydrogen /}$ metal atom ratio	Metal hydrides
Ref. 7	Hydriding: $\frac{dC}{dt} = A' \exp\left(-\frac{E_h}{RT}\right) \left(\frac{P}{P_{e,h}}\right)^a * \left[1 - \left(\frac{P_f}{P}\right)^a \left(\frac{C}{C_f}\right)^b\right]$ Dehydriding: $\frac{dC}{dt} = A' \exp\left(-\frac{E_d}{RT}\right) \left(\frac{C^b}{P_{e,h}^a}\right) * \left[1 - \left(\frac{P}{P_f}\right)^a \left(\frac{C_f}{C}\right)^b\right]$	Metal hydrides P_f and C_f are the “final” pressure and concentration in the solid (H/M ratio).

Appendices

Using the product / reactant information for each reaction given in Table 15, the general form of Equation 6 and considering the depletion of reactants:

for r_1

$$\left(\frac{dC_1}{dt}\right)_{r1} = D_1 \exp\left(-\frac{E_1}{RT}\right) * \left(\frac{P_{e,1} - P}{P_{e,1}}\right) * (C_2)^{\chi_1} \quad \text{and} \quad \left(\frac{dC_2}{dt}\right)_{r1} = -\left(\frac{dC_1}{dt}\right)_{r1}$$

for r_2

$$\left(\frac{dC_2}{dt}\right)_{r2} = D_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}}\right) * (C_1)^{\chi_2} \quad \text{and} \quad \left(\frac{dC_1}{dt}\right)_{r2} = -\left(\frac{dC_2}{dt}\right)_{r2}$$

for r_3

$$\left(\frac{dC_2}{dt}\right)_{r3} = D_3 \exp\left(-\frac{E_3}{RT}\right) * \left(\frac{P_{e,3} - P}{P_{e,3}}\right) * (C_3)^{\chi_3} \quad \text{and} \quad \left(\frac{dC_3}{dt}\right)_{r3} = -\left(\frac{dC_2}{dt}\right)_{r3}$$

for r_4

$$\left(\frac{dC_3}{dt}\right)_{r4} = D_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}}\right) * (C_2)^{\chi_4} \quad \text{and} \quad \left(\frac{dC_2}{dt}\right)_{r4} = -\left(\frac{dC_3}{dt}\right)_{r4}$$

Recall from Figure 145 the three pressure regimes, denoted by index s :

$s = 1$	$P < P_{e,a}$:	r_1 and r_3 active
$s = 2$	$P_{e,a} < P < P_{e,b}$:	r_2 and r_3 active
$s = 3$	$P_{e,b} < P$:	r_2 and r_4 active

For a hydriding kinetics run in pressure regime 3,

$$\begin{aligned} \left(\frac{dC_2}{dt}\right)_{r2} &= D_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}}\right) * (C_1)^{\chi_2} \quad \text{and} \quad \left(\frac{dC_1}{dt}\right)_{r2} = -\left(\frac{dC_2}{dt}\right)_{r2} \\ \left(\frac{dC_3}{dt}\right)_{r4} &= D_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}}\right) * (C_2)^{\chi_4} \quad \text{and} \quad \left(\frac{dC_2}{dt}\right)_{r4} = -\left(\frac{dC_3}{dt}\right)_{r4} \end{aligned}$$

Adding the composition evolution rates for each active reaction type,

$$\begin{aligned} \frac{dC_1}{dt} &= \left(\frac{dC_1}{dt}\right)_{r2} = -D_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}}\right) * (C_1)^{\chi_2} \\ \frac{dC_2}{dt} &= \left(\frac{dC_2}{dt}\right)_{r2} + \left(\frac{dC_2}{dt}\right)_{r4} \\ &= D_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}}\right) * (C_1)^{\chi_2} - D_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}}\right) * (C_2)^{\chi_4} \end{aligned}$$

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$$\frac{dC_3}{dt} = \left(\frac{dC_3}{dt} \right)_{r4} = D_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}} \right) * (C_2)^{\chi_4}$$

Initial conditions are also required, such as

$$C_1^{t=0} = 1, C_2^{t=0} = 0, C_3^{t=0} = 0$$

The heat source for regime 3 will be

$$q_{s=3} = \Delta \tilde{H}_a \rho \left(\frac{dC_2}{dt} \right)_{r2} + \Delta \tilde{H}_b \rho \left(\frac{dC_3}{dt} \right)_{r4}$$

11.1.3 Reaction Rate Equations with Saturation Compositions

The form of Equation 5 is able to represent non-ideal capacities, but only if the hydrogen saturation levels are independent of temperature. Making the scaling parameter, ν , temperature dependent would not be physically realistic or result in a model which is valid for arbitrary temperature histories. For this, any temperature dependence related to final capacity must be located in the rate equations. This was modeled by introducing temperature dependent saturation compositions, $C_k^{sat}(T)$. These variables represent the residual reactant levels at the hydriding saturation point for different temperature values. The resulting composition factors are changed to:

$$f_C = (C_k - C_k^{sat}(t))^{\chi_i} \text{ if } C_k - C_k^{sat}(T) \geq 0$$

$$f_C = 0 \text{ if } C_k - C_k^{sat}(T) < 0$$

The rate equations are represented accordingly by:

Equation 7

$$\frac{dC_1}{dt} = -A_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}} \right) * [C_1 - C_1^{sat}(T)]^{\chi_2}$$

$$\frac{dC_2}{dt} = A_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P - P_{e,2}}{P_{e,2}} \right) * [C_1 - C_1^{sat}(T)]^{\chi_2} - A_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}} \right) * [C_2 - C_2^{sat}(T)]^{\chi_4}$$

$$\frac{dC_3}{dt} = A_4 \exp\left(-\frac{E_4}{RT}\right) * \left(\frac{P - P_{e,4}}{P_{e,4}} \right) * [C_2 - C_2^{sat}(T)]^{\chi_4}$$

The compositions after completion of hydriding are:

$$C_1 = C_1^{sat}(T), \quad C_2 = C_2^{sat}(T), \quad C_3 = 1 - C_1^{sat}(T) - C_2^{sat}(T)$$

and the total H₂ absorption capacity is:

$$w_{iso}^{sat}(T) = 0.0187 * C_2^{sat}(T) + 0.056 * (1 - C_1^{sat}(T) - C_2^{sat}(T))$$

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11.2 Derivation of System Scaling Model

In the current section, relationships are derived to scale the gravimetric and volumetric efficiencies of a system.

11.2.1 Gravimetric Efficiency

To derive a relationship relating gravimetric efficiencies for two configurations, a number of assumptions need to be made on what will remain constant between the two tank configurations.

The primary assumptions are

1. Each tank will store the same *hydrogen mass*, m_H .
2. Each tank will have the same *powder fill fraction*,

Equation 8

$$f = \frac{V_{p1}}{V_{t1}} = \frac{V_{p2}}{V_{t2}}$$

where V_{p1} is the volume of powder 1 and V_{t1} is the internal tank volume for the system with powder 1. The subscripts with 2 are for powder 2.

3. Each tank will have the same *system density*,

Equation 9

$$\rho_s = \frac{m_{t1}}{V_{t1}} = \frac{m_{t2}}{V_{t2}}$$

where m_{t1} is the mass of the tank with powder 1. This assumes that each tank will have the *same operation pressure and heat transfer rate requirements*. If the powders differ substantially in pressure requirements or in heat transfer enhancement (different hydrogen capacities per unit volume or enthalpy), then additional scaling corrections will be required.

The two types of *hydride powder* will have:

- Different powder mass densities,

Equation 10

$$\rho_{p1} = \frac{m_{p1}}{V_{p1}}$$

Equation 11

$$\rho_{p2} = \frac{m_{p2}}{V_{p2}}$$

where m_{p1} is the mass of powder 1.

- Different powder H_2 weight capacities,

Equation 12

$$w_{p1} = \frac{m_H}{m_{p1}}$$

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Equation 13

$$w_{p2} = \frac{m_H}{m_{p2}}$$

- Different powder H₂ densities,

$$\gamma_{p1} = \frac{m_H}{V_{p1}}$$

$$\gamma_{p2} = \frac{m_H}{V_{p2}}$$

Of the three variables, ρ_{p1} , w_{p1} and γ_{p1} , only two are independent since,

$$w_{p1} * \rho_{p1} = \frac{m_H}{m_{p1}} * \frac{m_{p1}}{V_{p1}} = \frac{m_H}{V_{p1}} = \gamma_{p1}$$

$$\gamma_{p1} = w_{p1} * \rho_{p1} \quad [\text{kg H}_2 / \text{m}^3] = [\text{kg H}_2 / \text{kg CCH}] * [\text{kg CCH} / \text{m}^3]$$

There is limited data which indicates that the volumetric density of hydrogen for a variety of storage materials is roughly constant, $\gamma_{p2} \approx \gamma_{p1}$.

The two *systems* will have:

- Different gravimetric efficiencies relative to the powder mass,

Equation 14

$$W_1 = \frac{m_{p1}}{m_{T1}} = \frac{m_{p1}}{m_{t1} + m_{p1}}$$

Equation 15

$$W_2 = \frac{m_{p2}}{m_{T2}} = \frac{m_{p2}}{m_{t2} + m_{p2}}$$

where m_{T1} is the total mass of the powder and tank for the #1 system.

- Different gravimetric efficiencies relative to the hydrogen mass,

Equation 16

$$G_1 = \frac{m_H}{m_{T1}} = \frac{m_H}{m_{t1} + m_{p1}}$$

Equation 17

$$G_2 = \frac{m_H}{m_{T2}} = \frac{m_H}{m_{t2} + m_{p2}}$$

Of the three variables w_{p1} , W_1 and G_1 only two are independent since

$$w_{p1} * W_1 = \frac{m_H}{m_{p1}} * \frac{m_{p1}}{m_{t1} + m_{p1}} = \frac{m_H}{m_{t1} + m_{p1}} = G_1$$

or

$$G_1 = w_{p1} * W_1$$

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For the gravimetric efficiency relative to powder mass, we desire to obtain an expression for W_2 and this quantity depends on m_{p2} and m_{t2} as indicated in Equation 15. From Equation 13,

Equation 18
$$m_{p2} = \frac{m_H}{w_{p2}}$$

From Equation 12,

Equation 19
$$m_H = w_{p1} * m_{p1}$$

Substituting Equation 19 into Equation 18,

Equation 20
$$m_{p2} = \frac{w_{p1}}{w_{p2}} m_{p1}$$

which gives one of the needed variables in Equation 15 in terms of the variables for configuration 1 and the powder properties of configuration 2. The other variable for which we need to substitute is m_{t2} . We can solve for this in Equation 9,

Equation 21
$$m_{t2} = \frac{V_{t2}}{V_{t1}} m_{t1}$$

From Equation 8,

Equation 22
$$\frac{V_{t2}}{V_{t1}} = \frac{V_{p2}}{V_{p1}}$$

Combining Equation 10 and Equation 11,

Equation 23
$$\frac{V_{p2}}{V_{p1}} = \frac{m_{p2}}{m_{p1}} \frac{\rho_{p1}}{\rho_{p2}}$$

Substituting Equation 23 into Equation 22 and then Equation 22 into Equation 21,

Equation 24
$$m_{t2} = \frac{m_{p2}}{m_{p1}} \frac{\rho_{p1}}{\rho_{p2}} m_{t1}$$

Rearranging Equation 20,

Equation 25
$$\frac{m_{p2}}{m_{p1}} = \frac{w_{p1}}{w_{p2}}$$

Substituting Equation 25 into Equation 24,

Equation 26
$$m_{t2} = \frac{w_{p1}}{w_{p2}} \frac{\rho_{p1}}{\rho_{p2}} m_{t1}$$

Putting Equation 20 and Equation 26 into Equation 15,

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$$\text{Equation 27} \quad W_2 = \frac{m_{p2}}{m_{t2} + m_{p2}} = \frac{\frac{w_{p1}}{w_{p2}} m_{p1}}{\frac{w_{p1}}{w_{p2}} \frac{\rho_{p1}}{\rho_{p2}} m_{t1} + \frac{w_{p1}}{w_{p2}} m_{p1}} = \frac{m_{p1}}{\frac{\rho_{p1}}{\rho_{p2}} m_{t1} + m_{p1}}$$

Note that both m_{p2} and m_{t2} are proportional to w_{p1} / w_{p2} , so that an increase in the weight percent of hydrogen stored in powder 2 will decrease both the powder mass as well as the estimated tank mass, resulting in an unchanged gravimetric efficiency W_2 .

If we rearrange Equation 14, we obtain

$$\text{Equation 28} \quad m_{t1} = \frac{1 - W_1}{W_1} m_{p1}$$

Substituting Equation 28 into Equation 27,

$$\text{Equation 29} \quad W_2 = \frac{m_{p1}}{\frac{\rho_{p1}}{\rho_{p2}} \frac{1 - W_1}{W_1} m_{p1} + m_{p1}}$$

Canceling m_{p1} from the numerator and denominator,

$$\text{Equation 30} \quad W_2 = \frac{1}{1 + \frac{\rho_{p1}}{\rho_{p2}} \frac{1 - W_1}{W_1}}$$

As a check, if we set $\rho_{p1} = \rho_{p2}$ in Equation 30, we get

$$W_2 = \frac{1}{1 + \frac{1 - W_1}{W_1}} = \frac{1}{\frac{W_1 + 1 - W_1}{W_1}} = \frac{1}{\frac{1}{W_1}} = W_1$$

as expected. We can also divide Equation 30 by W_1 to obtain

$$\text{Equation 31} \quad \frac{W_2}{W_1} = \frac{1}{W_1 + \frac{\rho_{p1}}{\rho_{p2}} (1 - W_1)}$$

Thus, given the assumptions above for scaling system 2 when changing from powder 1 to powder 2, the gravimetric efficiency only depends on the ratio of the powder densities and not on the weight fraction of hydrogen stored in the powder.

Another form of Equation 31 is

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Equation 32

$$W_2 = \frac{W_1}{W_1 + \frac{\rho_{p1}}{\rho_{p2}}(1 - W_1)} = \frac{1}{1 + \frac{\rho_{p1}}{\rho_{p2}}\left(\frac{1}{W_1} - 1\right)}$$

or

$$\frac{1}{W_2} = 1 + \frac{\rho_{p1}}{\rho_{p2}}\left(\frac{1}{W_1} - 1\right)$$

or

$$\frac{\rho_{p1}}{\rho_{p2}} = \frac{\left(\frac{1}{W_2} - 1\right)}{\left(\frac{1}{W_1} - 1\right)}$$

Equation 33

which is a more mathematically symmetric equation relating the two configurations.

For the gravimetric efficiency relative to hydrogen stored, we substitute Equation 20 and Equation 26 into Equation 17,

Equation 34

$$G_2 = \frac{m_H}{\frac{w_{p1}}{w_{p2}} \frac{\rho_{p1}}{\rho_{p2}} m_{t1} + \frac{w_{p1}}{w_{p2}} m_{p1}} = \frac{w_{p2}}{w_{p1}} * \frac{m_H}{\frac{\rho_{p1}}{\rho_{p2}} m_{t1} + m_{p1}}$$

Rearranging Equation 16,

Equation 35

$$m_{t1} = \frac{m_H}{G_1} - m_{p1}$$

Substituting Equation 35 into Equation 34, then factoring out m_{p1} in the denominator and applying Equation 12,

$$\begin{aligned} G_2 &= \frac{w_{p2}}{w_{p1}} * \frac{m_H}{\frac{\rho_{p1}}{\rho_{p2}} \left(\frac{m_H}{G_1} - m_{p1} \right) + m_{p1}} = \frac{w_{p2}}{w_{p1}} * \frac{m_H / m_{p1}}{\frac{\rho_{p1}}{\rho_{p2}} \left(\frac{m_H}{m_{p1} * G_1} - 1 \right) + 1} \\ &= \frac{w_{p2}}{w_{p1}} * \frac{w_{p1}}{\frac{\rho_{p1}}{\rho_{p2}} \left(\frac{w_{p1}}{G_1} - 1 \right) + 1} \end{aligned}$$

Finally, canceling w_{p1} from the numerator and denominator,

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Equation 36

$$G_2 = \frac{w_{p2}}{\frac{\rho_{p1}}{\rho_{p2}} \left(\frac{w_{p1}}{G_1} - 1 \right) + 1}$$

(Equation 36 could be obtained also by simply multiplying Equation 32 by w_{p2} .)

After some additional calculations, it was observed that another form can be obtained quickly by multiplying Equation 33 by w_{p1} / w_{p2} ,

$$\frac{w_{p1}}{w_{p2}} \frac{\rho_{p1}}{\rho_{p2}} = \frac{w_{p1}}{w_{p2}} \frac{\left(\frac{1}{W_2} - 1 \right)}{\left(\frac{1}{W_1} - 1 \right)} = \frac{\left(\frac{1}{W_2 / w_{p2}} - \frac{1}{w_{p2}} \right)}{\left(\frac{1}{W_1 / w_{p1}} - \frac{1}{w_{p1}} \right)} = \frac{\left(\frac{1}{G_2} - \frac{1}{w_{p2}} \right)}{\left(\frac{1}{G_1} - \frac{1}{w_{p1}} \right)}$$

Recalling that $\gamma_p = w_p * \rho_p$

Equation 37

$$\frac{\gamma_{p1}}{\gamma_{p2}} = \frac{\left(\frac{1}{G_2} - \frac{1}{w_{p2}} \right)}{\left(\frac{1}{G_1} - \frac{1}{w_{p1}} \right)}$$

or

Equation 38

$$G_2 = \frac{1}{\frac{1}{w_{p2}} + \frac{\gamma_{p1}}{\gamma_{p2}} \left(\frac{1}{G_1} - \frac{1}{w_{p1}} \right)}$$

Equation 38 has been implemented in the embedded Excel spreadsheet of Table 17. If reading the MicroSoft Word version of the report, you can double click the table to enter new input values.

Table 17: Example values / spreadsheet to calculate G_2 .

w_p1	0.0127
gamma_p1	49.5
G_1	0.008382
w_p2	0.023
gamma_p2	33
G_2	0.009585621

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From the form of Equation 37, it is obvious that if $w_{p2} = w_{p1}$ and $\gamma_{p2} = \gamma_{p1}$, then $G_2 = G_1$.

Thus, the gravimetric density relative to hydrogen stored G_2 is increased as the weight percent of hydrogen in powder 2, w_{p2} , is increased and also as the density ρ_{p2} is increased.

Assuming,

$$\gamma_{p1} = \gamma_{p2}$$

Equation 39

$$w_{p1}\rho_{p1} = w_{p2}\rho_{p2}$$

or

Equation 40

$$\frac{\rho_{p1}}{\rho_{p2}} = \frac{w_{p2}}{w_{p1}}$$

The result of Equation 40 can be inserted into Equation 31 to obtain

Equation 41

$$\frac{W_2}{W_1} = \frac{1}{W_1 + \frac{w_{p2}}{w_{p1}}(1 - W_1)}$$

Equation 31 or Equation 41 are plotted in Figure 146 for W_1 values of 0.4, 0.6 and 0.8. Note that decreasing powder 2 density or increasing powder 2 hydrogen weight percent reduces the system gravimetric efficiency. If we take powder 1 to be NaAlH_4 and powder 2 to be a goal material

$$\frac{w_{p2}}{w_{p1}} = \frac{7.5\%}{5.5\%} = 1.36$$

Figure 146: Plot of the change in gravimetric efficiency versus relative powder density (or relative hydrogen weight percent if $\gamma_{p1} = \gamma_{p2}$).

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Comparing with a Savannah River National Laboratory (SRNL), formerly known as the Savannah River Technology Center (SRTC) design based on LaNi_5 , $W_1 = 0.66$, $\rho_{p1} = 3.6 \text{ g/cc}$, Equation 32 becomes,

Equation 42

$$W_2 = \frac{1}{1 + \frac{3.6}{\rho_{p2}} \left(\frac{1}{0.66} - 1 \right)}$$

Plotting Equation 42, we obtain Figure 147. For the SRTC material,

$$\gamma_{p1} = w_{p1} * \rho_{p1} = 0.0127 \text{ kg H}_2 / \text{kg} * 3600 \text{ kg} / \text{m}^3 = 49.5 \text{ kg H}_2 / \text{m}^3$$

For NaAlH_4 with the a typical powder density,

$$\gamma_{p2} = w_{p2} * \rho_{p2} = 0.055 \text{ kg H}_2 / \text{kg} * 600 \text{ kg} / \text{m}^3 = 33 \text{ kg H}_2 / \text{m}^3$$

From Equation 38 with $G_1 = w_{p1} * W_1$,

$$G_2 = \frac{1}{\frac{1}{0.055} + \frac{49.5}{33} \left(\frac{1}{0.0127 * 0.66} - \frac{1}{0.0127} \right)} = 0.0127$$

Plotting Equation 38 with $\gamma_{p1} = \gamma_{p2}$ and the SRTC system as configuration 1, we have Figure 148

$$G_2 = \frac{1}{\frac{1}{w_{p2}} + \frac{1}{G_1} - \frac{1}{w_{p1}}} = \frac{1}{\frac{1}{w_{p2}} + \frac{1}{W_1 * 0.0127} - \frac{1}{0.0127}}$$

Plotting this equation for different values of W_1 is shown in Figure 149.

Figure 147: Plot of W_2 from Equation 42 with SRTC design as configuration 1.

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Figure 148: Plot of G_2 for SRTC value of $W_1 = 0.66$ assuming $\gamma_{p1} = \gamma_{p2}$.

Figure 149: Plot of G_2 for multiple W_1 assuming $\gamma_{p1} = \gamma_{p2}$.

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11.2.2 Volumetric Efficiency

The relationships for volumetric efficiencies are much simpler. The only additional assumption that should be made is that the ratio

Equation 43

$$r = \frac{V_{t1}}{V_{T1}} = \frac{V_{t2}}{V_{T2}}$$

of internal tank volume V_t to total package volume, V_T , is constant. This means that the spacing between tanks, conformability, etc. is the same for the two configurations.

The volumetric efficiency relative to the powder volume is defined as

$$E_1 = \frac{V_{p1}}{V_{T1}}$$

Splitting the right hand side into two factors and recalling Equation 8 and Equation 43,

$$E_1 = \frac{V_{p1}}{V_{t1}} \frac{V_{t1}}{V_{T1}} = f * r$$

which is constant from the assumptions made so that

$$E_1 = E_2 = E .$$

A second volumetric efficiency should be defined relative to the *amount of hydrogen*, similar to the distinction between W_i and G_i . We could choose the *amount of hydrogen* to be either the standard volume of hydrogen stored or its mass. By choosing mass, we do not need to define any new constants. Therefore, the volumetric efficiency relative to hydrogen is

$$F_1 = \frac{m_H}{V_{T1}}$$

Splitting this up into factors which have been previously defined,

Equation 44

$$F_1 = \frac{m_H}{V_{p1}} * \frac{V_{p1}}{V_{t1}} * \frac{V_{t1}}{V_{T1}} = \gamma_{p1} * f * r = \gamma_{p1} * E$$

Similarly,

Equation 45

$$F_2 = \gamma_{p2} * E$$

Taking the ratio of Equation 44 and Equation 45,

$$\frac{F_2}{F_1} = \frac{\gamma_{p2} * E}{\gamma_{p1} * E} = \frac{\gamma_{p2}}{\gamma_{p1}} .$$

or

$$F_2 = \frac{\gamma_{p2}}{\gamma_{p1}} F_1$$

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As expected, increasing the value of γ_{p2} has a direct effect on the system volumetrics.

11.3 Heat Transfer Liquid Figure of Merit

To start off, we will consider some basic heat transfer quantities that are used primarily in formulas for heat transfer and pressure drop. These formulas are usually empirical and are based on reducing experimental data taken under a variety of conditions.

Reynolds number (Ref. 9, p. 170) is defined as

$$\text{Re} = \frac{\rho V D_h}{\mu} = \frac{V D_h}{\nu}$$

where ρ is density, V is (average) velocity, D_h is hydraulic diameter, μ is viscosity and $\nu = \mu / \rho$ is the kinematic viscosity.

The Hydraulic diameter (Ref. 9, p. 232) is

$$D_h = \frac{4A_c}{P}$$

where A_c is cross sectional area and P is the wetted perimeter of the pipe or flow channel. Note that for the case of a circular cross section, we get the expected result of

$$D_h = \frac{4\pi r^2}{2\pi r} = 2r$$

and we also have

$$A_c = \frac{\pi}{4} D_h^2$$

The Prandtl number is a fluid property,

$$\text{Pr} = \frac{c_p \mu}{k}$$

The Nusselt number (Ref. 9, p. 191) is

$$\text{Nu} = \frac{h D_h}{k}$$

with the properties evaluated at the fluid bulk temperatures. Rearranging this,

$$h = \frac{\text{Nu } k}{D_h}$$

For fully developed turbulent flow in smooth tubes, these dimensionless numbers are related by (Ref. 9, p. 226):

Equation 46
$$\text{Nu} = 0.023 \text{Re}_d^{0.8} \text{Pr}^n$$

where $n = 0.4$ for heating and 0.3 for cooling. As a simplification, we will use 0.35 for both since the fluid will be used for heating and cooling. Combining formulas, the convective heat transfer coefficient becomes

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$$h = 0.023 * \left(\frac{\rho V D_h}{\mu} \right)^{0.8} \left(\frac{c_p \mu}{k} \right)^{0.35} \frac{k}{D_h}$$

Equation 47

$$h = 0.023 \frac{(\rho V)^{0.8} k^{0.65} c_p^{0.35}}{D_h^{0.2} \mu^{0.45}}$$

The typical relationship for pressure drop is (Ref. 9, p. 231),

Equation 48

$$\Delta P = f * \left(\frac{L}{D_h} \right) * \frac{1}{2} * \rho * V^2$$

The friction factor, f , captures the complexity of the fluid and flow including the effect of viscosity. For laminar flow,

Equation 49

$$f = \frac{64}{\text{Re}} = \frac{64\mu}{\rho V D_h}$$

and

$$\Delta P = \frac{64\mu}{\rho V D_h} * \left(\frac{L}{D_h} \right) * \frac{1}{2} * \rho * V^2 = 32\mu * \left(\frac{L}{D_h^2} \right) * V$$

For turbulent flow of smooth tubes,

Equation 50

$$f = \frac{0.316}{\text{Re}^{0.25}} = 0.316 * \left(\frac{\mu}{\rho V D_h} \right)^{0.25}$$

and

$$\Delta P = 0.316 * \left(\frac{\mu}{\rho V D_h} \right)^{0.25} * \left(\frac{L}{D_h} \right) * \frac{1}{2} * \rho * V^2 = 0.158 * \mu^{0.25} * \left(\frac{L}{D_h^{1.25}} \right) * \rho^{0.75} * V^{1.75}$$

For pumping power,

$$\dot{W} \left[\frac{Nm}{s} \right] = \Delta P A_c V = \Delta P \frac{\dot{m}}{\rho} \left[\frac{N}{m^2} \frac{kg/s}{kg/m^3} \right]$$

If we use the symbol

$$\text{volume flow rate} = F = A_c V = \frac{\dot{m}}{\rho}$$

then,

$$\dot{W}_{ideal} = \Delta P * F$$

where the “ideal” subscript indicates that this is for a pump with 100% efficiency.

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Both the heat transfer and the pumping power will increase as the velocity or mass flow rate of the fluid is increased. One measure of fluid performance is to divide the heat transfer by the pumping power. While it is possible that the pressure level of the pump (higher pressure/lower flow rate versus a lower pressure/higher flow rate with equal power) could affect its efficiency and cost, we will assume this is negligible and just examine the pumping power of the fluid. We will term η_h the convective heat transfer efficiency which gives the heat transfer per degree of temperature difference divided by the pumping power and has units of [1 / deg. C],

$$\eta_h = \frac{h * A}{\dot{W}} = \frac{\text{heat transfer per deg}}{\text{pumping power}} \left[\frac{W / m^2 C * m^2}{W} = \frac{1}{C} \right]$$

where A is the surface area associated with the convective heat transfer, i.e. the surface area of the tubing inner diameter, D . For a circular tube, $D = D_h$ and

$$A = \pi D_h L.$$

We can substitute in for the quantities to determine how η_h depends on the fluid properties and other quantities. In general,

$$\eta_h = \frac{h * A}{W} = \frac{h * A}{\Delta P A_c V} = \frac{h * \pi D_h L}{\Delta P \frac{\pi}{4} D_h^2 V} = \frac{4h * L}{\Delta P D_h V} = \frac{4h * L}{f * \left(\frac{L}{D_h} \right) * \frac{1}{2} * \rho * V^2 D_h V} = \frac{8h}{f * \rho * V^3}$$

The convection coefficient h and friction factor f require empirical fits to experiment. Substituting in the relations for turbulent flow given above,

$$\eta_h = \frac{8h}{f * \rho * V^3} = \frac{8 * 0.023 \frac{(\rho V)^{0.8} k^{0.65} c_p^{0.35}}{D_h^{0.2} \mu^{0.45}}}{0.316 * \left(\frac{\mu}{\rho V D_h} \right)^{0.25} * \rho * V^3}$$

Thus, for turbulent flow in smooth circular tubes,

Equation 51

$$\eta_h = 0.582 * \left(\frac{\rho^{0.05} k^{0.65} c_p^{0.35}}{\mu^{0.70}} \right) * \left(\frac{D_h^{0.05}}{V^{1.95}} \right)$$

The convective heat transfer efficiency is split into those factors that are related to fluid properties and those that are not. The efficiency is insensitive to fluid density and tube diameter, is mildly dependent on specific heat, has moderate dependence on thermal conductivity & viscosity, and is strongly dependent on velocity.

If the pumping power is very low, then we will not care about these sensitivities, but as we push the flow rate to maximize the convective heat transfer, the pumping power and the sensitivities in the formula for η_h will become important.

From Equation 51, we can use the grouping

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$$\chi \equiv \left(\frac{\rho^{0.05} k^{0.65} c_p^{0.35}}{\mu^{0.70}} \right)$$

to evaluate which fluid will be best for achieving the maximum heat transfer for a given pumping power.

11.4 Calculations for Cost Modeling

The cost calculations associated with the discussion in Section 4.3 are detailed in this appendix for each major component in the storage system.

Composite vessel: \$300 to \$600

- Based on preliminary quotations by a composite vessel manufacturer, Carlton, that produces many vessels for paintball, fire suppression and other high quantity applications, initial estimates for a vessel which could hold nominally 5 kg of H₂ are: 1 tank = \$600; 3 tanks = 3*\$420 = \$1260, 9 tanks = 9*\$300 = \$2700 for 10,000 tanks per year. From this information, we can deduce the trend that keeping the total volume of the vessel(s) constant, the cost (for a fixed system quantity) scales with the number of vessels per system approximately as

$$C = N^{2/3}$$

- If the system is made with 3 tanks (11" diameter, 70% dense powder, 40" length. 4 wt% aluminum foam) and using $L = 0.90$,

$$\$1260 * \left(\frac{1,000,000}{10,000} \right)^{\log 0.90 / \log 2} = \$625$$

or about half of the price for 10,000 units per year.

- If the system is made with 1 tank (17" diameter, 70% dense powder, 48" length. 4 wt% aluminum foam),

$$\$600 * \left(\frac{1,000,000}{10,000} \right)^{\log 0.90 / \log 2} = \$300$$

- The cost for the carbon fiber is around \$10 per pound, but could drop to an estimated \$7 per pound for higher quantities or lower with current manufacturing oriented development projects. Estimates indicate that $\frac{3}{4}$ of the vessel weight could be the carbon fiber. Carlton numbers (closer to a high quantity product) indicate the composite shell including polar bosses will weigh between 33 (1 tank) and 48 lbs (3 tanks). This is a carbon fiber cost of between \$173 ($33 * \frac{3}{4} * 7$) and \$360 ($48 * \frac{3}{4} * 10$). These are reasonable at roughly half of the above total vessel costs.

Heat exchanger tubing: \$80 to \$160

- Based on the Prototype 1 heat exchanger design, there would be 24 passes per vessel with 5 vessels per system that are 3.5 feet long each. This gives $3.5 * 24 * 5 = 420$ ft of tubing per system.
- A preliminary quotation of \$1.70 per ft was obtained for 300 ft.

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- Yearly large scale quantity would be $1,000,000 \text{ units} * 420 \text{ ft} / \text{unit} = 420,000,000 \text{ ft}$. Using an L value of 0.93,

$$\$1.70 \text{ per foot} * \left(\frac{420,000,000}{300} \right)^{\log 0.93 / \log 2} = \$1.70 * 0.227 = \$0.39 \text{ per foot}$$

- $\$0.39 * 420 = \164 .
- Price negotiations could result in a lower effective L value than 0.93 or alternately a lower quotation for 300 ft. Thus, it is estimated that the cost be reduced by as much as half.

Particle filter: \$45 to \$135

- A lower cost alternative to porous stainless steel filters are fiberglass/screen ones. Estimates by Kaydon gave costs of \$8 for an area of 14 square inches and quantity of 3000. Each foot in length of a 0.5" diameter filter will have 19 square inches.
- For the filter, the raw material costs are secondary to the manufacturing costs, so it is estimated that the L proportion will 0.88. Extrapolating from a quantity of 3000 to 1,000,000 and from a size of 14 to 19 square inches:

$$\frac{19}{14} * \$8 * \left(\frac{1,000,000}{3000} \right)^{\log 0.88 / \log 2} = \$3.72 \text{ per foot}$$

- Depending on the number of tanks, mass flow within the hydride and other internal features to assist mass flow, the number of filters could range from an estimated 4 to 12 where each is three feet long.
- Thus, the total cost ranges from \$45 to \$135

Heat transfer enhancement, \$90

- Foam, aluminum, \$6000
 - ERG: \$1 per in³, 100 liters = 6120 in³
 - Quantity extrapolations would lower cost, but the basic process is complex and expensive.
- Screen, aluminum, \$90
 - Estimate need for 200 ft² per unit
 - Quotation for 900 ft² is \$1.34 per ft
 - Scaling up to 1,000,000 units per year using $L = 0.94$ gives a cost of

$$\$1.34 * \left(\frac{200,000,000}{900} \right)^{\log 0.94 / \log 2} = \$0.45 \text{ per ft}^2$$

Valve and pressure relief device, \$20 to \$50

- \$17, based on cost estimation report for compressed hydrogen gas storage system.
- Possibility of a separate valve for each vessels: $3 \text{ vessels} * \$10 = \30 .

Heat transfer oil: \$15 to \$25

- Estimate between 2 to 3 gallons of oil per system.
- 3000 gallons of ParaTherm MR oil costs \$18 per gallon
- 2 million gallons per year is estimated to be less than half of this,

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$$\left(\frac{2,000,000}{3000} \right)^{\log 0.93 / \log 2} = 0.51$$

or \$7 to \$9 per gallon.

Water / Oil heat exchanger: \$30

- Sizing will depend on pressure drop and temperature difference of liquids.
- Without specific sizing, discussion with FlatPlate, Inc. on their brazed plate heat exchangers gives an estimate of \$40 for OEM heat exchangers. Increasing quantity to 1 million per year will bring this down to an estimated \$30.

Oil pump: \$30

- Conversation with D.L. Thurrott, Inc. who developed an inexpensive pump for an automotive application that was \$73. The customer then had the pumps custom built by another manufacturer for \$22.

NaAlH₄ Hydride Material: \$1250 to \$2500

- 5 kg H₂ / 4 wt % capacity = 125 kg of NaAlH₄.
- High quantity cost estimate by Albemarle Corporation of \$10 to \$20 per kg of NaAlH₄.

11.5 High Level System Modeling for Materials Evaluation

As mentioned in Section 6.3, the high level model does not track time dependent behavior of the material with high resolution. Rather, the hydrogen weight fraction w or effective capacity is determined at a specific time t_w from material test data for different pressures and temperatures, $w(T, P)$. An example of idealized $w(T, P)$ data is given in the left hand graph of Figure 150. The time t_w is essentially the refueling time and should be chosen by the user based on inspection of the material data. Note that the model approximates the reaction rate to be constant over time t_w so that reasonable time points would be those in the region where the fastest kinetics curve just begins to saturate, i.e. in the knee of the curve.

We will take the hydrogen pressure to be constant within the system but will consider how the temperature varies for the hydride as heat is dissipated to a working fluid circulating within tubes or channels. We will also have the temperature distribution be linear with respect to hydride mass and use the symbol ΔT to denote the magnitude of this linear distribution. Extensions to the modeling could incorporate exponential temperature distributions that are observed in FEA results, but the linear approximation will capture the first order effects. For the hydride throughout the system, its temperature variation causes a variation in effective capacity $w(T, P)$ from point to point. In the solution method, an average effective capacity for all of the hydride, $\bar{w}(\Delta T, P)$, is calculated for different ΔT magnitudes as detailed below. Here, the overbar on $\bar{w}$ denotes the notion of average. The associated $\bar{w}(\Delta T, P)$ curves are shown in the right hand graph of Figure 150. We then apply this reformulated material data in the solution method by first calculating the temperature difference

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ΔT from heat transfer relations and then evaluating $\bar{w}(\Delta T, P)$ to estimate the average hydride weight fraction within the system.

Figure 150: Left – fabricated material data $w(T, P)$. Right - Processed data $\bar{w}(\Delta T, P)$.

Ultimately, we seek to calculate the system weight fraction w_{sys} which depends on various masses. For the material, the mass will be denoted with an (h) subscript for hydride, a portion of which is the Hydrogen (H) mass. To keep the model somewhat generic and be applicable to a variety of system designs, the primary system component masses are labeled according to their function whether they support pressure only (po) i.e. the vessel, heat exchange only (xo) such as fins or foam or pressure and heat exchange (px) as for the working fluid tubing or channels. Finally, a placeholder is included for other components (o) including supports, insulation, working fluid, etc.

$$w_{sys} = \frac{m_H}{m_h + m_{po} + m_{px} + m_{xo} + m_o}$$

The model equations are derived using variables which depend on system size for ease in both derivation and subsequent interpretation. However, the equations involve the ratio of extensive variables and so produce results which are independent of system size. We begin calculation of the different masses by fixing the system interior volume arbitrarily as $V_{po} = 0.1 \text{ m}^3$ (100 liters or about 25 gal). The hydrogen pressure P and heat-exchange-only mass m_{xo} are inputs that will be varied to determine their optimum values. Most of the model equations involve simple bookkeeping of system masses and volumes. The hydrogen mass is calculated from the hydride mass and average weight fraction $\bar{w}$,

$$m_H = \bar{w} * m_h$$

Calculation of the average material capacity $\bar{w}$ is dependent on the temperature distribution within the heat exchanger and will be discussed in detail subsequently. The hydride mass depends on the specified powder density ρ_h and hydride powder volume V_h ,

$$m_h = \rho_h * V_h$$

The hydride volume V_h is close to the interior volume V_{po} with a minor correction for the total heat exchanger volume,

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$$V_h = V_{po} - V_x$$

The heat exchanger volume V_x is not the outer envelope volume but the volume which displaces the hydride. The heat exchanger volume is comprised of the px and xo portions,

$$V_x = V_{xo} + V_{px}$$

The xo volume is determined by the specified mass m_{xo} and the xo material (fin / foam) density,

$$V_{xo} = m_{xo} / \rho_{xo}$$

The px volume is associated with tubing or working fluid channels. In this model, we do not include convection and detailed heat exchanger design optimization explicitly, so the px volume is estimated by scaling the px volume fraction

$$f_{px} \equiv V_{px} / V_{po}$$

proportionately with the average heat generation body heat flux $\bar{b}$ (having units of W/m^3) that depends on the enthalpy $\Delta\tilde{H}$ (energy per mass rather than per mole), the average weight fraction rate $\dot{\bar{w}}$ and the hydride density,

$$\bar{b} \equiv \Delta\tilde{H} * \dot{\bar{w}} * \rho_h$$

such that

$$\frac{f_{px}}{f_{px}^{ref}} = \frac{\bar{b}}{\bar{b}^{ref}}$$

More detailed heat exchanger models are use to determine the reference values f_{px}^{ref} and $\bar{b}^{ref}$. Combining,

$$V_{px} = V_{po} * f_{px}^{ref} \frac{\bar{b}}{\bar{b}^{ref}}$$

To evaluate $\bar{b}$, we need to make an initial guess for $\dot{\bar{w}}$ and update its value to converge iteratively on a solution. For the initial guess, we can use the peak value of the weight fraction rate from the materials kinetics data,

$$\dot{\bar{w}}_{initial} = \dot{w}_{peak}$$

Having an estimate for $\dot{\bar{w}}$, we calculate $\bar{b}$, then V_{px} , then V_x , then V_h and finally m_h . For the po component (pressure vessel), we approximate that the mass is proportional to the pressure rating and interior volume:

$$m_{po} = C_{po} * P * V_{po}$$

A similar relation is also used for the px mass,

$$m_{px} = C_{px} * P * V_{px}$$

The mass of other components, m_o will vary considerably with system design and is not closely related to hydride material properties. We will estimate this here using a constant mass fraction f_o ,

$$m_o = f_o * (m_h + m_{po} + m_{px} + m_{xo})$$

What then remains is to determine the average effective capacity $\bar{w}$. We first continue with the discussion of calculating $\bar{w}(\Delta T, P)$ from $w(T, P)$ and then turn to the calculation of ΔT .

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For the best system performance, we want to locate the hydride temperature distribution ΔT such that it gives the highest average capacity. In this simplified analysis, we will assume that thermal management at the refueling station can position the ΔT as desired. We will also assume that the effective capacity curves versus temperature, i.e. at fixed pressure, $w(T, P_{fixed})$ are symmetric about the peak w , so that the highest average capacity will occur when the ΔT band is centered on temperature of peak w . However, there is an upper temperature limit to the absorption reaction. To capture this, when the upper temperature in a centered ΔT band reaches a specified value (140 C or less in Figure 150), this temperature is fixed and only the lower temperature of the band is allowed to change. Given this guidance on the ΔT distribution location, the average capacity is then calculated,

$$\bar{w}(\Delta T, P) = \frac{1}{\Delta T} \int_{T_{low}}^{T_{high}} w(T, P) * dT \quad \text{with} \quad \Delta T = T_{high} - T_{low}$$

If the points in the $w(T, P)$ data are evenly spaced with temperature, then the calculations can be simplified to a common numeric average.

We now need to estimate the hydride temperature distribution ΔT associated with heat transfer that depends on refueling time t_w , heat exchanger mass m_{xo} and other quantities. We will consider primarily the temperature difference that occurs due to conduction through the xo portion of the heat exchanger (fins or foam), denoted by ΔT_c . In general, other sources of temperature variability $\Delta \tilde{T}$ could be included due to such things as nonuniformity of density and transient effects giving $\Delta T = \Delta T_c + \Delta \tilde{T}$, but these will not be detailed in the present model so that

$$\Delta T = \Delta T_c$$

This will produce optimistic system performance estimates but still should reveal reasonable estimates for the influence of material properties. The magnitude of the temperature difference occurring within the hydride filled heat exchanger can be estimated starting with the functional form for one dimensional steady state heat conduction,

$$q = \Delta \tilde{H} * \dot{\bar{w}} * m_h = \frac{\Delta T_c}{R_{overall}}$$

To develop the variable dependencies and approximate functional form, we could take the heat transfer to be comprised of two steps in series: 1) short range conduction of heat through a hydride powder layer or cell to the conduction enhancement (fin or foam) and 2) long range conduction of heat through the conduction enhancement to the working fluid tubing or channel. This would produce an overall resistance that is the sum of the two individual resistances,

$$R_{overall} = R_{sr} + R_{lr}$$

where R_{sr} is inversely proportional to the hydride powder thermal conductivity k . However, results from FEA analyses of finned heat exchanger designs revealed that this influence of k was too strong, indicating the conduction process is not well approximated by the two steps in series. Using the FEA results, a modified form was developed for the temperature distribution of the hydride,

$$\Delta T_c = \bar{b} * \left(\frac{k_{ref}}{k} \right)^x \left(\frac{C_{lr}}{m_{xo} / V_h} \right)$$

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The best estimate for x was 0.2 over a range of k from 0.1 to 5 W/m C. The value of k_{ref} is 0.5 W/m C. Estimates for the long range heat transport constant C_{lr} varied from 1e-3 to 3e-3 deg. C / (W/kg) depending on whether the thermal contact resistance between powder and fin was taken to be uniform or vary spatially between high and low values. Other parameter values are given in Table 18.

With the estimate of ΔT_c , $\bar{w}$ can be interpolated from $\bar{w}(\Delta T, P)$ to then calculate m_H and w_{sys} .

Table 18: Model parameters.

Parameter	Value	Units
$w(T, P)$	Material specific	kg / kg
t_w	Material specific	s
k	Material specific	W/m C
f_{px}^{ref}	0.035	m ³ / m ³
$\bar{b}^{ref}$	5*10 ⁵	J/s m ³
x	0.2	--
k^{ref}	0.5	J / s m C

Parameter	Value	Units
$\Delta \tilde{H}$	Material specific	J / kg
ρ_h	Material specific	kg/m ³
C_{po}	2e-5 to 3e-5	kg / Pa m ³
C_{px}	1.5e-4	kg / Pa m ³
f_o	0.05	kg / kg
C_{lr}	1e-3 to 3e-3	C / (W/kg)
ρ_{xo}	2700	kg/m ³

The model derived above estimates the system capacity w_{sys} for the specified material properties as well as the input conditions of pressure P and xo mass m_{xo} . To determine the optimum input conditions and system performance, the model should be evaluated over a range P and m_{xo} values and the optimum values selected at the maximum w_{sys} .