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

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E. Hartford, CT

Project ID #ST4

Merit Review
Arlington, VA
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Overview

- **Timeline**
  - 4/1/02 Start
  - 9/30/06 End
  - 60% Complete
- **Budget**
  - $3.8M Total Program
    - $2.7M DoE
    - $1.1M (27%) UTC
  - $0.5M DoE FY'04
  - $0.8M DoE FY'05
- **Barriers**
  - Gravimetric Density: 2KWh/kg
  - Volumetric Density: 1.5 kWh/l
  - Charging rate: 1.5 kgH_2/min.
  - Discharging rate: 4 gH_2/sec.
  - Safety: Meets or exceeds applicable standards
  - Durability: 1000 cycles
- **Partners**
  - UTC Fuel Cells
  - U. Hawaii
  - HCI
  - Albemarle
  - QuesTek LLC
  - Spencer Comp.

Objective

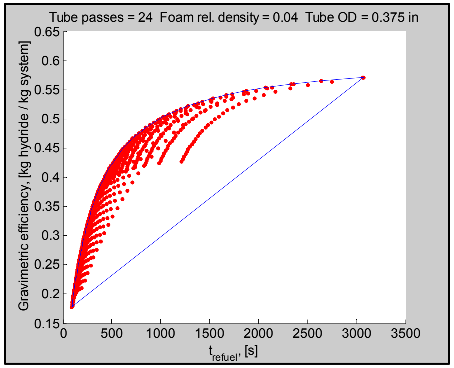
Design build and evaluate prototype low pressure hydrogen storage systems initially utilizing catalyzed $NaAlH_4$, but capable of being altered to use "*any*" reversible chemical hydride, having the higher gravimetric and/or volumetric hydrogen storage densities with minimal redesign.

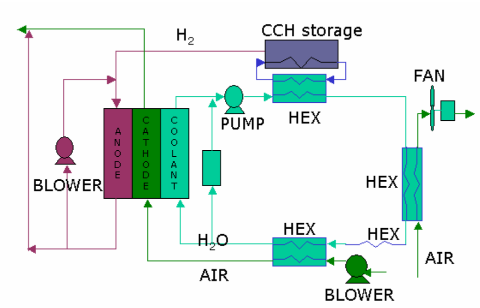
- Assess the utility of combined atomistic/thermodynamic modeling in predicting the effectiveness of potential catalysts.
- Characterize $NaAlH_4$ to obtain the highest performance composition and high volume media synthesis methods.
- Develop an understanding of the safety testing protocols and engineering design requirements for utilizing alanate materials.
- Develop, build & demonstrate an in-situ rechargeable 1 kg hydrogen storage system.

Approach

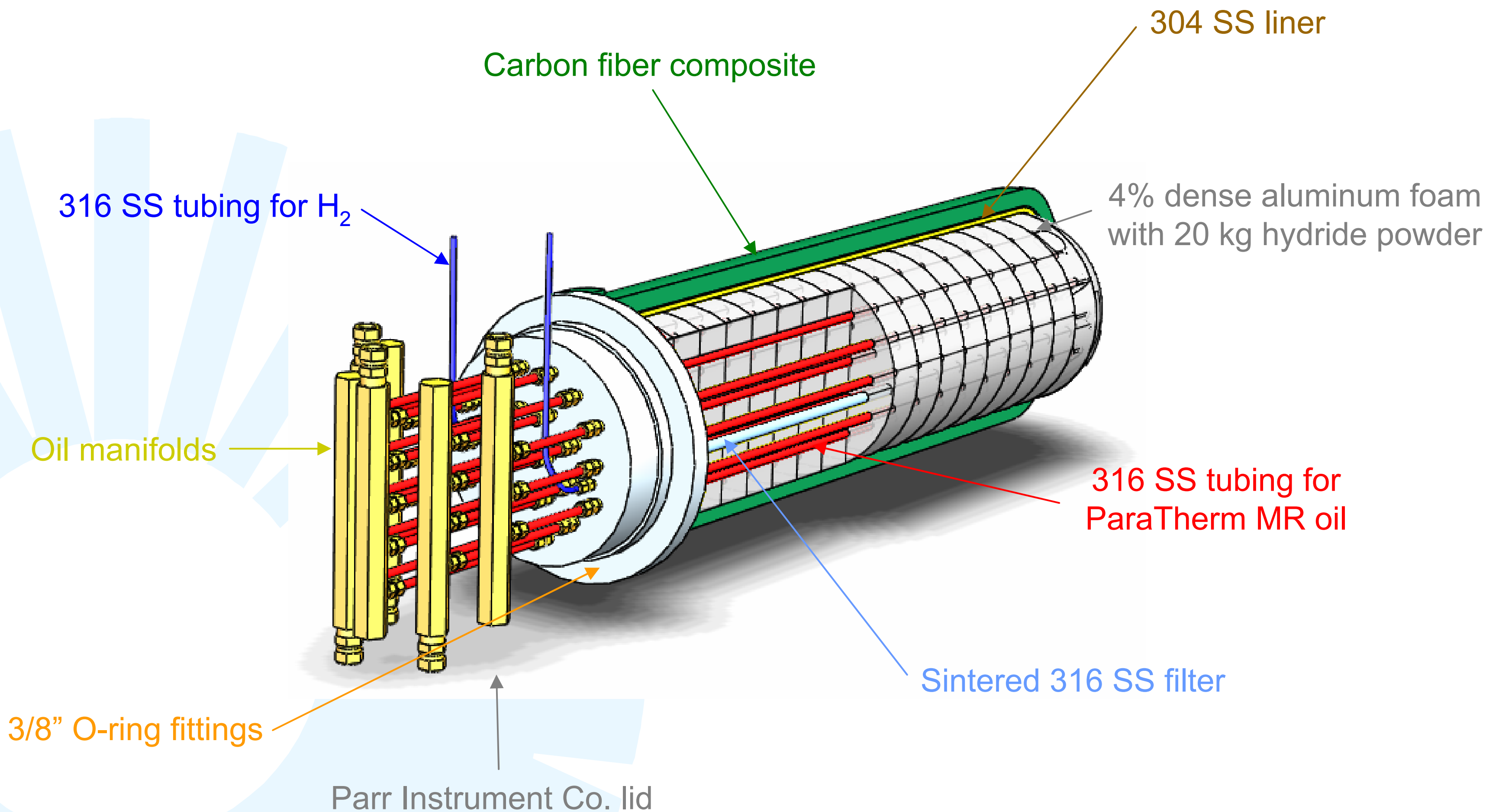
Concurrent System Design

- Identify new technical challenges including
  - Media packing
  - Media processing scale-up
  - Safety
  - Heat transfer specifics
- Quantify system limits for different system approaches. (ex. < 15 min refueling increasingly costly for in situ charging of $NaAlH_4$).
- Inform the materials community of system trade-offs to guide selection of the best media (effects of charging pressure, density, temperature span).
- Time targets – minimize the delay between materials and prototype development in the future.
- Examine fuel cell systems integration issues.





First Prototype Overview



High Throughput Synthesis

Requirement: **30 kg** of catalyzed media

Process	Batch size	Frequency & g's	Time & temperature
SPEX Mill (SM)	0.005 kg	16 Hz 40 g	3 hrs 57 C
Tumble Mill (TM)	2 x 0.5 kg	1 Hz 1 g	24 hrs 23 C
Power Mill (PM)	0.5 kg	10 Hz 15 g	1 hr 40 C

- Initial tests showed similar kinetics for PM TiF_3 and SM $TiCl_3$.
- Subsequent tests indicated batch-to-batch variation for PM processing with kinetics between 60% and 90% of small scale processing.
- Scale-up media processing is challenging to obtain both high throughput processing and high kinetics.

SPEX Mill

Tumble Mill

30 kg Catalyzed $NaAlH_4$

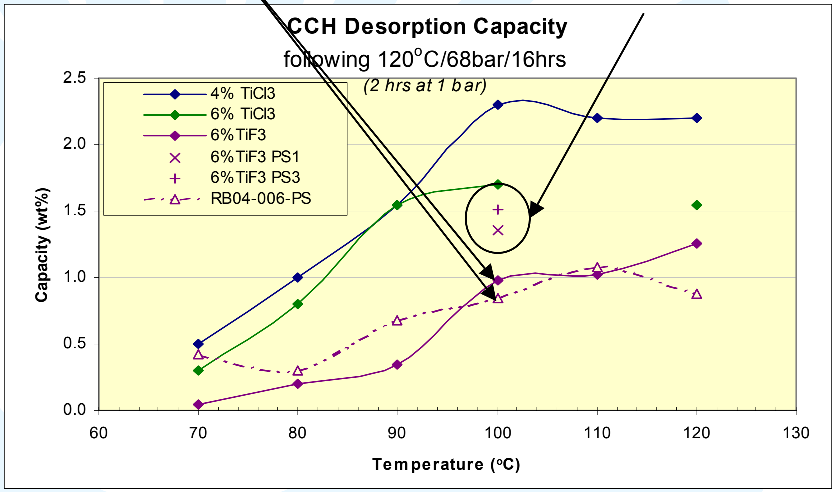
Media Quality Evaluations

- Media composition commercially pure $NaAlH_4$ supplied by Albemarle & catalyzed with 6m/o TiF_3
- Large batch processing results in significantly lowered kinetics due to lowered mechanico-chemical reaction as a result of lower kinetic energy pre mass input.
- Batch-to-batch variation in kinetics is significant and needs to be closely monitored and controlled.
- **System performance will be base-lined with reference to known compound kinetics.**

Kinetic Analysis Quality Assurance

Subsequent Batch Analysis

Initial batch trials using high volume attrition unit.



Compositional Analysis Quality Assurance by XRD

Large Quantity Processing

$NaAlH_4$ + 6m% TiF_3

Batch Check XRD Results

TM Tumble Mill 20 hrs
PSX Paint Shake X hrs.

Charged 120C/68bar/16hr
Discharged 120C/1bar/20hr

XRD Results *(mol%)*

Batch ID	$NaAlH_4$	α-Na_3AlH_6	β-Na_3AlH_6	NaH	Al	TiF_3	NaF	AlH_3	Condition
Tumble Milled									
RB04-006	63.4	0.0	1.9		34.6	0.2			TM
RB04-007	75.1	0.0	1.9		23.1	0.0			TM
RB04-008	70.7	0.0	**23.0**		26.9	0.2			TM
RB04-026	52.3	0.0	5.8		**41.9**	0.3			TM
RB04-030	71.9	1.0	2.0		25.1	1.0			TM
RB04-033	70.5	0.0	1.9		25.6	**2.0**			TM
RB04-049	72.3	1.4	0.9		22.8	**2.7**			TM
average	*68.0*	*0.3*	*5.3*		*28.6*	*0.9*			
RB04-006	22.6	2.0	15.4		59.9	0.1			TM+Chg+DChg
RB04-007	28.1	1.5	13.7		57.6	0.1			TM+Chg+DChg
RB04-008	**37.1**	0.0	**29.2**		**25.6**	**1.2**		2.1	TM+Chg+DChg
RB04-026									
RB04-030	34.3	0.0	14.5		51.1	0.1			TM+Chg+DChg
RB04-033	**45.0**	0.0	8.3		46.7	0.04			TM+Chg+DChg
RB04-049									
average	*33.4*	*0.7*	*16.2*		*48.2*	*0.3*		*0.4*	

Media Densification Screening Tests

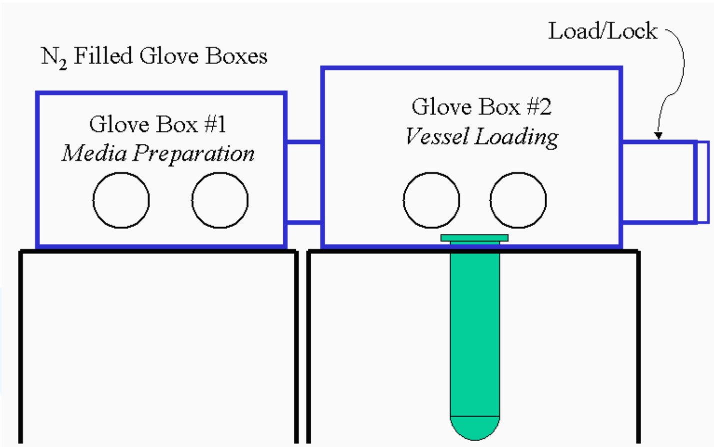
Initial estimate

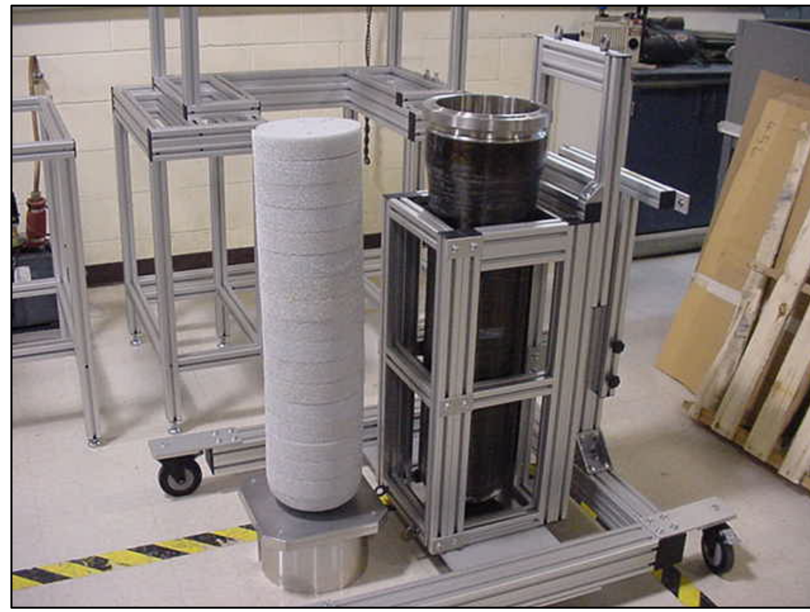
Method	g/cc	Scale up	Kinetics
M1	**0.44 to 0.80**	Moderate	**Good**
M2	0.97 to 1.07	Poor	Good
M3	0.44	Poor	Moderate to Good
M4	0.92	Good	Poor
M5	***0.6 to 0.75***	***Good***	***Good***

All experiments with aluminum foam

- **Densification method M5 was initially chosen to be scaled up for construction of the first prototype.**
- **Method of densification changed to M1 after scale up issues of M5 posed significant schedule delay.**

Assembly Approach & Hardware





Significant resources were invested in assuring a safe & clean environment for system loading

Powder Loading & Disk Installation

Foam disks filled with hydride

1

Move to assembly glove box

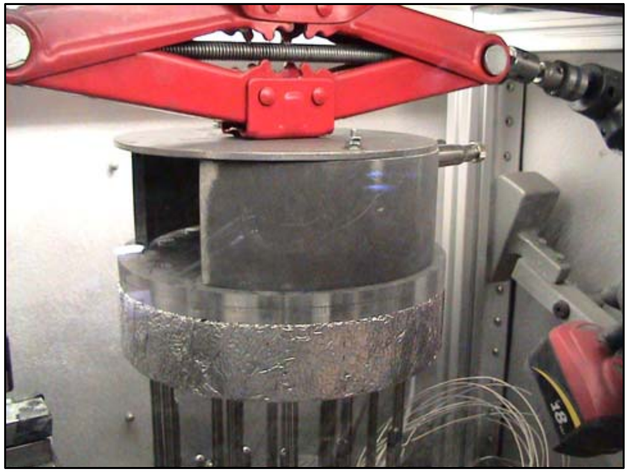
2

Alignment of disk with tubes

3

Press fit disk into vessel

4



System Loading Results

Bottom two sections
- **installed empty**
- **filled by shaking the entire vessel.**

$$\rho \approx 0.35 \text{ g/cc}$$

Nominal 1" gap present due to disk binding

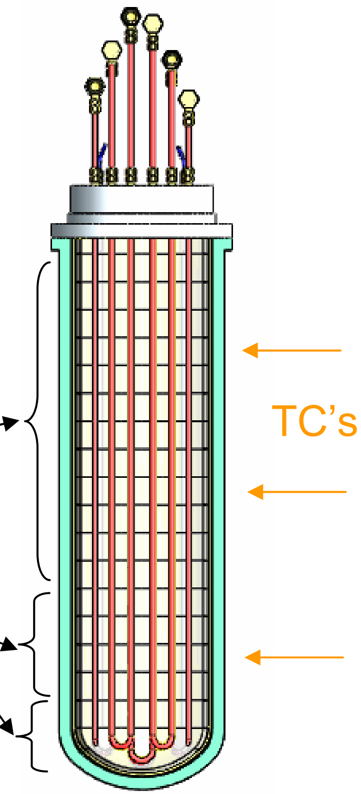
Scaled-up M5 approach

$$\rho \approx 0.4 \text{ g/cc}$$

Modified M1 method developed

$$0.4\text{g/cc} > \rho > 0.6 \text{ g/cc}$$

Entire vessel
- **19 kg of hydride**
- **Average hydride density = 0.44 g/cc**



12 internal thermocouples installed in three disks

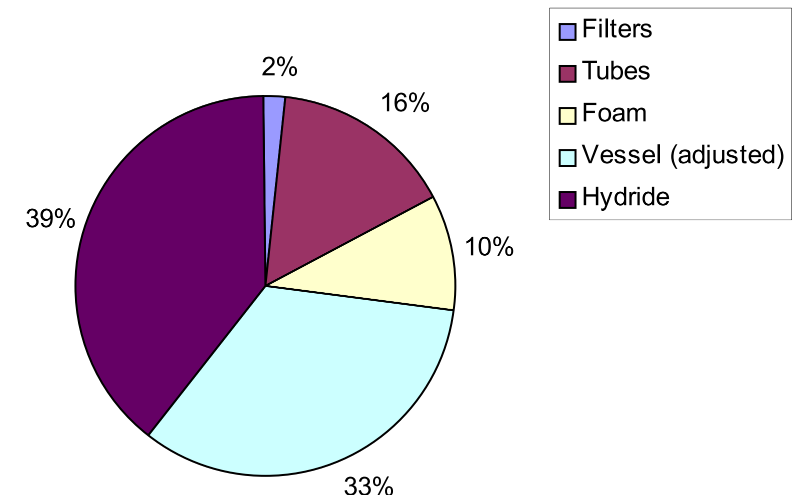
Powder loading in an inert environment is challenging with overall density of 0.44g/cc (35% ρ_{th}) achieved.
Densification will be examined at full scale for 2nd prototype.

Component Masses

Actual & Projected

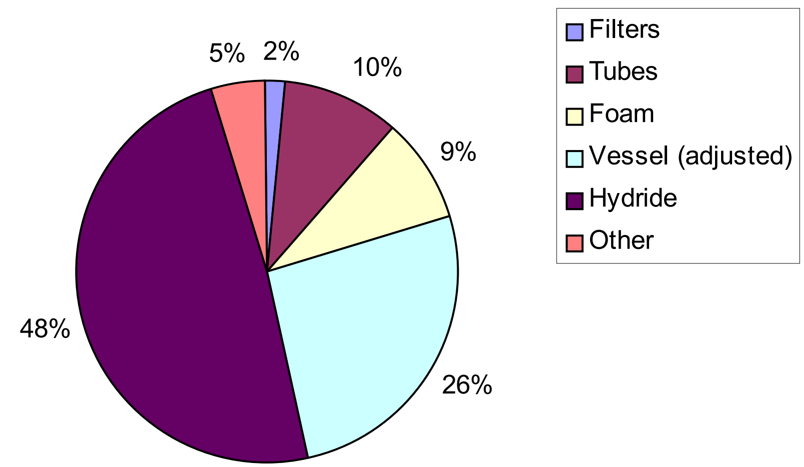
Actual storage tank

- 19 kg hydride in system
- 0.44 g/cc average hydride density
- 0.60 g/cc peak hydride density for disk
- 100 atm vessel
- Assumes hemispherical domed end



Projected storage tank

- Eliminate tubing excess Factor of Safety
- Eliminate vessel excess Factor of Safety
- Apply best settled density of 0.6 g/cc for entire vessel resulting in 26 kg hydride
- Add oil, insulation, supports, …
- Gravimetric efficiency of 48%

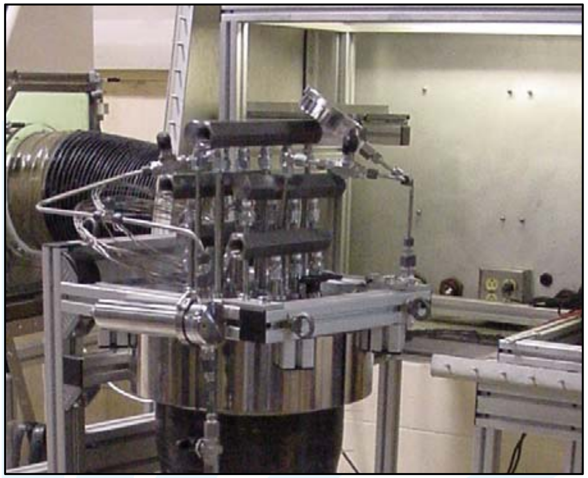


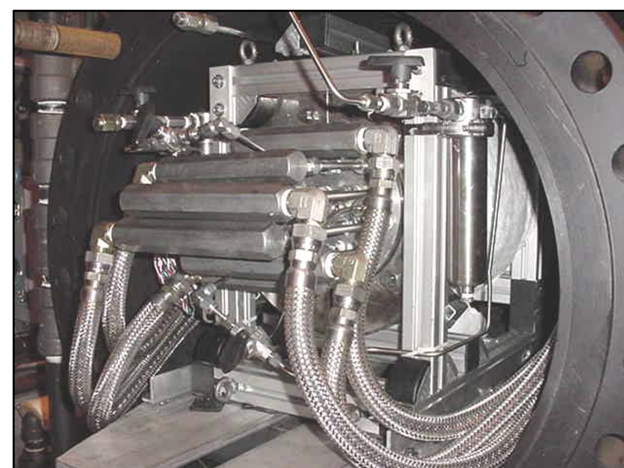
Gravimetric engineering efficiency, E^g_f of ~50% achieved.

Final Assembly and Installation

Final assembly of manifold
Transport to test cell

Application of external insulation
Installation into containment



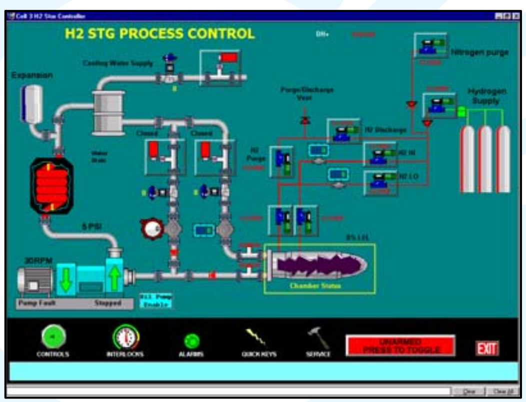


Evaluation System Development

Features

- 12kW electric oil heater
- Oil/water HX oil cooler
- 100gpm max variable speed, 650F, 350 psi oil pump & sealed reticulating system
- Secondary containment with inert gas blanket and H_2 monitor.
- Two range H_2 mass flow measurement
- 12 vessel & 15 system type K TC's
- 2 vessel and 4 system 2000psi pressure transducers.
- 6 strain gages
- Data acquisition at 1-100 Hz
- Automated control software with fail safe shut down.

> Significant resources were invested in system evaluation facilities assuring: accurate, controlled, <u>safe</u> and cost effective evaluation.



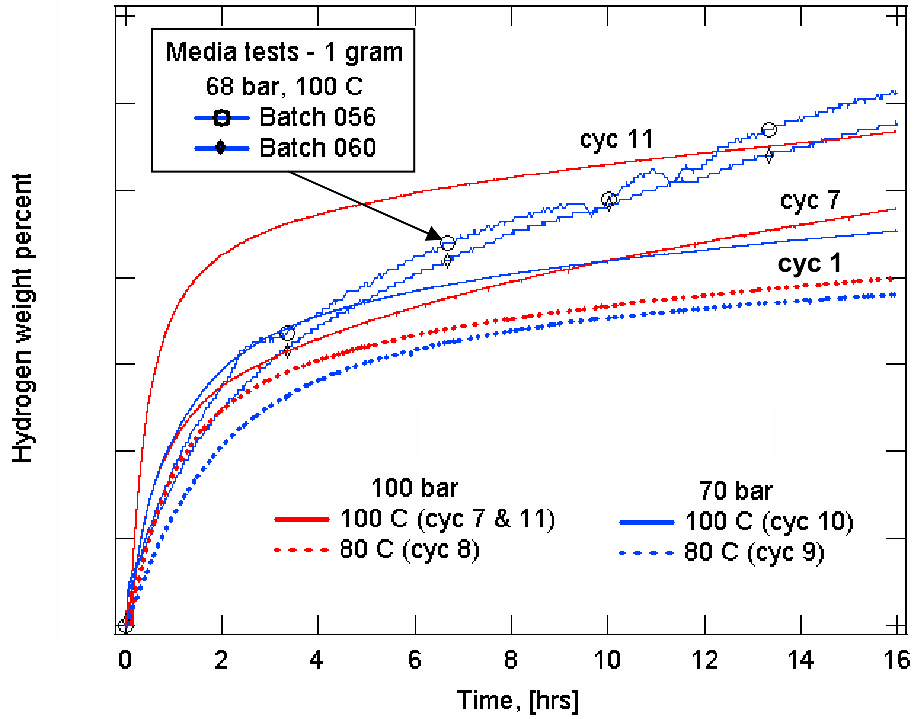
CCHSS#1 Evaluation Results

Charging
- Std. discharge: 150°C/vac./24hrs.
- 70 and 100 bar charging (24 hrs):
  - 80 °C ✓
  - 100 °C ✓
  - 120 °C

Discharging
- Std. charge: 100°C/100bar/24hr
- 2 bar discharging (24 hrs)
  - 80 °C
  - 90 °C ✓
  - 100 °C ✓
  - 110 °C

Control Dynamics
- Optimum charging

CCHSS#1 Charging Tests



- **Initial absorption data are consistent with 1 gram tests for scaled up media processing.**
- **Prototype fabrication & testing have had little effect on kinetics.**
- **Kinetics and capacity are improving with cycling probably due to increased homogenization of Ti^{+3} catalyst**

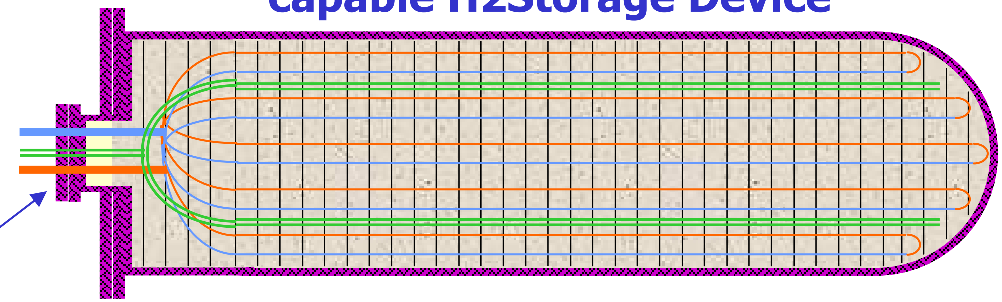
Future Work

Second Prototype

Address challenges for realizing a prototype system with low weight hemi-spherical end closure having small boss port and improved gravimetrics:

- Improved media composition, 4wt.%
- Improved media synthesis method
- New media filling method to obtain ρ >.6 g/cc
- Advanced tube/fin HX
- Internal manifold

Intermediate 100 bar capable H2Storage Device

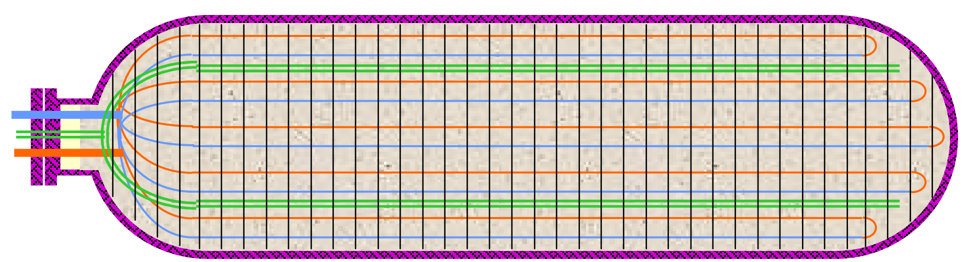


Modify new lid to mimic opening of boss port composite vessel domed end

Methods and design will allow media to be loaded into system with **prefabricated HX** through **reduced diameter opening** and be applicable to **other media**.

Approach will simplify fabrication logistics allowing emphasis on critical technologies.

Ultimate 100 bar capable H2Storage Device

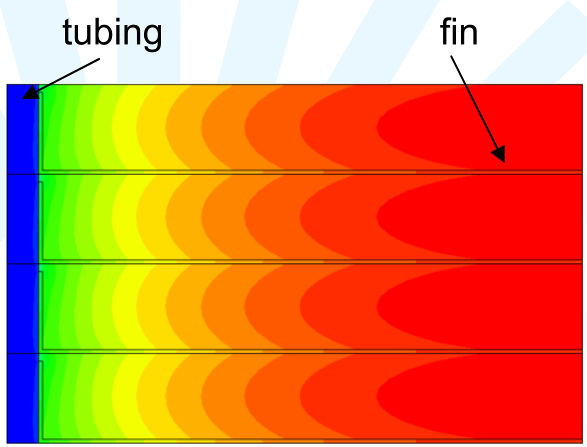


Second Prototype Finned HX

Advantages of finned HX over aluminum foam

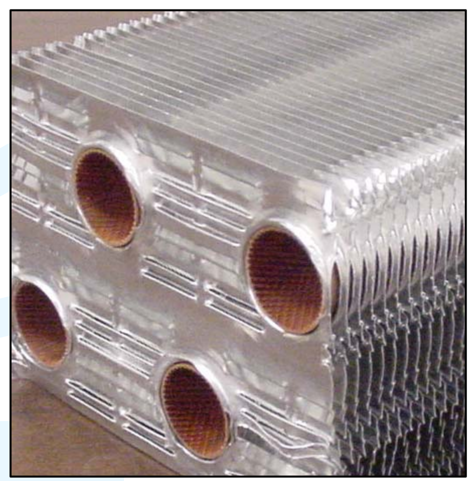
- **Improved long range heat transport (up to 3X better)**
- **Lower cost for mass production**
- **More adaptable to a variety of powder loading methods**

Automated ABAQUS 2D simulation



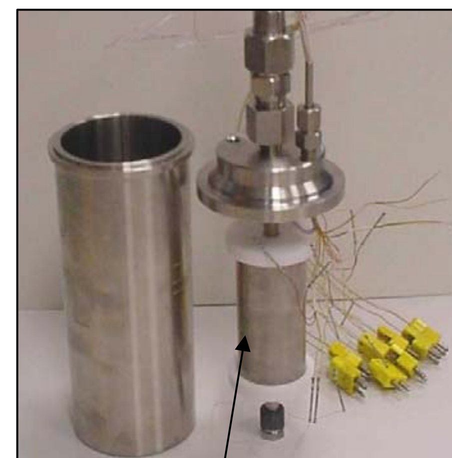
Simulated temperature contours during charging

Conventional Tube/Fin Heat Exchanger



Carrier

Perform initial development on subscale 4” diameter fins



Replace with fin stack

System Projections

	Symbol	units	system #1	system #1.1	system #2	system #2P	system #2PP	DoE 2007 Goal	DoE 2010 Goal	DoE 2015 Goal
	Media		CCHSS#1 6%TiF3	CCHSS#1.1 6%TiF3	CCHSS#2					
Media Density	ρ^m	g/cm^3	1.51	1.51	1.51	1.51	1.51			
Media Gravimetric Density	ρ^m_g	wt%	0.035	0.035	**0.04**	**0.065**	**0.075**			
Media Volumetric Density	ρ^m_v	kgH_2/m^3	52.9	52.9	60.4	98.2	113.3			
System Gravimetric Density	ρ^s_g	wt%	1.4%	1.7%	2.2%	4.5%	6.0%	**4.5%**	**6.0%**	**9.0%**
	ρ^s_g	*kWh/kg*	*0.5*	*0.6*	*0.7*	*1.5*	*2.0*	*1.5*	*2.0*	*3.0*
System Volumetric Density	ρ^s_v	kgH_2/m^3	11.7	17.2	24.3	46	53	**36**	**45**	**81**
	ρ^s_v	*kWh/l*	*0.39*	*0.57*	*0.81*	*1.53*	*1.77*	*1.2*	*1.5*	*2.7*
Gravimetric Engineering Efficeincy	E^g_f		0.39	**0.48**	**0.55**	**0.69**	**0.80**			
Volumetric Engineering Efficiency	E^v_f		0.65	0.65	**0.67**	**0.67**	**0.67**			
Powder Packing density	ρ^m_p		0.34	**0.5**	**0.6**	**0.7**	**0.7**			

system
media

Two hemispherical ends
Optimized external heat exchange

Eliminate excess factors of safety
Best large scall powder packing acheived

Increase gravimetric efficiency 7 pts.
Increased Media Gravimetrics 0.5wt%
Increase volumetric efficency 2 pts.
Increase powder packing 10 pts.

High capacity media
70 bar charging pressure
Optimal gravimetric efficency

Higher capacity media
50 bar charging pressure

Previous Year's Comments

- **Comment**

  "How to design a system such that it can be used with other metal hydrides?"

  With input of the heats of formation and chemical kinetics, maximum thermal loads are established which, through FEM and convex hull system optimization methods, guide heat exchanger design.

- **Comment**

  "Why are the results of the system level modeling sensitive IP?"

  The system level modeling utilized actual weights, volumes and performance metrics from the UTFuelCells Mercury Program, all of which are company owned and proprietary. Additionally, UTC is paying 27% cost share of the effort and a commercial rights agreement to all findings is in place with DoE.

- **Comment**

  "Alanates probably have limits and may never make DoE goals."

  $NaAlH_4$ alone will certainly never be able to meet the DoE 2010 and 2015 gravimetric goals, but it is anticipated that other systems, similar in chemistry and kinetics, will be discovered to meet these challenging requirements. By designing and fabricating a working system early in the technology development cycle, other less transparent technical barriers such as high volume media synthesis, media densification and long range heat transfer issues can be addressed. This should considerably shorten the design cycle allowing introduction of these new materials with minimal re-engineering.

Supplemental Slides

Publications

Articles

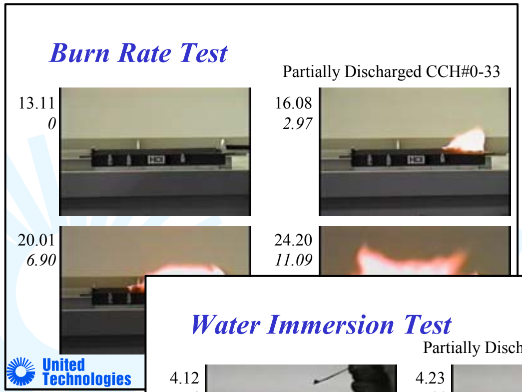
- C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," to be submitted to Phys. Rev. B.
- O. M. Lovvik and S. M. Opalka, "First-principles calculations of Ti-enhanced NaAlH4," Phys. Rev. B 71 054103-1-10 (2005).
- C. Qiu, G. B. Olson, S. M. Opalka and D. L. Anton, "A Thermodynamic Evaluation of the Al-H System," J. of Phase Equilibria and Diffusion -25(6) 520-527 (2004).
- D.L. Anton, "Hydrogen Desorption Kinetics in Transition Metal Modified $NaAlH_4$", J. Alloys and Compounds, 356-357, pp.400-4 (2003).
- 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).

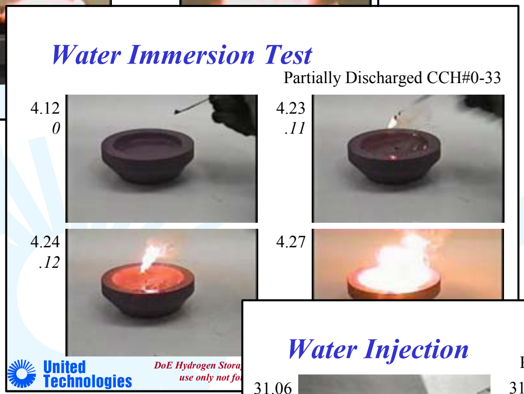
Presentations

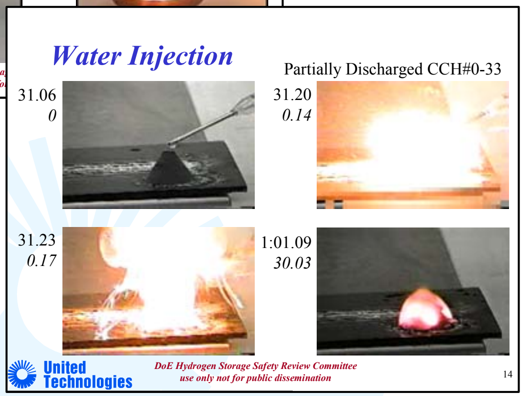
- Xia Tang, D. A. Mosher and D. L. Anton, "Practical Sorption Kinetics of $TiCl_3$ Doped NaAlH4" Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
- D. A. Mosher and D. L. Anton, "Beyond Weight Percent – The Influence of Material Characteristics on Hydrogen Storage System Performance," Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
- C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic Modeling of Sodium Alanates," Materials Science & Technology 2005 to be held in Pittsburgh, PA, on September 25-28, 2005.
- O. M. Løvvik and S. M. Opalka, "First-principles calculations of Ti-enhanced $NaAlH_4$." Presentation at the International Symposium of Metal Hydrogen Systems (MH2004), Krakow, Poland, September 10, 2004.
- S. M. Opalka and O. M. Lovvik, "Bulk Hydrogen Diffusion within Undoped and Titanium-Doped Sodium Alanate," and O. M. Lovvik and S.M. Opalka, "Calculation of hydrogen mobility near the surface of doped and undoped NaAlH4,"
- S. M. Opalka and D. L. Anton, "First principles study of sodium-aluminum-hydrogen," International Symposium On Metal Hydrogen Systems MH2002, Annecy, France, September 2-6, 2002.

Safety

Risk Identification







Fire risk quantitatively assessed

Dust Explosion Testing

•Dust explosion: class St-3, Highly Explosive when finely divided and dispersed.

	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/m³*	140	90	65	30
MIE *mJ*	<7	<7	110	17
T_c °C	137.5	137.5	584	430

P_{max} = maximum explosion pressure, R_{max} = pressure rise maximum, K_{st} = maximum scaled rate of pressure rise, MEC = minimum explosive concentration, MEI = minimum spark ignition energy, T_c = minimum dust cloud ignition temperature

United Technologies

DoE Hydrogen Storage Safety Review Committee use only not for public dissemination

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Explosion risks quantitatively assessed

Appendix V- UTRC Risk Assessment Form

Date	Room Number	Participants
5/4/04	S145H	Tom Ververis, Xia Tang, Ron Brown, Jodi Vecchiarelli

No	Process, Task or Step	Potential hazard	Controls in Place	Likelihood Occurrence	Potential Impact	Risk Rank	Controls Required To reduce risk further/Name/Date
1	Mixing Powder Media Preparation	Fire, Explosion	All work is done in glovebox filled with Nitrogen Containers inside glove box sealed Gloves inspected every day Nitrogen pressure checked every day Moisture and O2 sensor in glovebox Positive pressure maintained in glove box	2	3	6 Med	
2	Hydrogen Storage Running Test	Failure of High Pressure Systems Fire, Explosion	Restricted use Risk assessments Local rules and procedures Pressure rated components Pressure relief valves Automatic controllers; Redundant valves Detailed Procedures; Employee training Critical valve Maintenance Remote gas line shutoff and purge if loss of power or ventilation All test stands in hoods All equipment leak tested (H2 sniffer) Flash arrestor Moisture filters	2	3	6 Med	Lower Pressure
3	Hydrogen Storage, Running Test	High Temp. Oil Bath, Burns, Oil spill	Warning sign “Hot Oil” Secondary containment Redesigned Jack stand gard in place Located in hood.	2	2	4 Low	
4	Vacuum System (Hydrogen),Running Test	Explosion	Special Hydrogen Vac. Pumps Sparkless	2	3	6 Med	
5	Working in glovebox	Ergonomic pain	Limited time in glovebox to 45 minutes max. Set up to avoid awkward reaching	2	2	4 Low	
6	Lifting, transporting samples	Ergonomics	Training, procedures Weight kept to < 30 pounds	2	2	4 Low	

Comprehensive risk assessment performed on all major operations

Safety

Risk Mitigation

System loaded in inert gas

Media handled & stored under inert gas

System tested remotely

All risks reduced to low impact or negligible probability

Incoming material stored in fire cabinet

System housed and tested in secondary containment under inert gas