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

D. Mosher, X. Tang, S. Arsenault, B. Laube,
M. Cao, R. Brown, S. Saitta, J. Costello

United Technologies Research Center
East Hartford, Connecticut

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Overview

Objective: Identify and overcome the critical technical barriers in developing complex hydride based storage systems, especially those which *differ from conventional metal hydride systems*, to meet DOE system targets.

Approach: Design, fabricate and test a sequence of subscale and full scale prototypes involving material development such as safety assessment, catalysis and scaled-up processing.

Early systems development in parallel with novel materials research has been and will be important to hydrogen storage maturity.

Current Systems Focus

- On-board rechargeable
- Based on $NaAlH_4$ as representative complex hydride
- Generalize to materials which require moderate charging pressures

Program Plan

Completed
Under Way
Future Effort

- Safety Analysis
- Atomistic/Thermodynamic Modeling
- 50g H_2 Prototype System
- Media Kinetic Characterization & Modeling
- Heat/Mass Transfer Analysis
- High Temp. Composite Tank Development
- Component Fabrication
- Assembly System Fabrication
- Evaluation Facility Development
- 1kg H_2 CCHSS#1 Assembly
- CCHSS#1 Evaluation

- CCHSS#1 Model Validation
- CCHSS#2 System Design
  - *Advanced HX design*
  - *New media filling method*
  - *Compact manifold*
- Enhanced Media
  - *Advanced catalyst concepts*
  - *High volume synthesis method*
- CCHSS#2 Prototype
  - *Fabrication*
  - *Performance Testing*
  - *Model Validation*
- $NaAlH_4$ System Neutralization
  - *Process development*
  - *Prototype 1 decommissioning*
- New Materials
  - Powder densification

Program tasks nearing completion.

Review of Prototypes

	$LaNi_5$	$NaAlH_4$
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

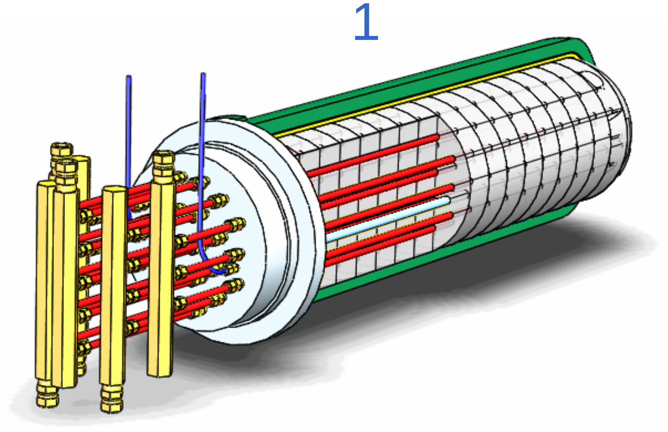
** 50% powder relative density, 4% H_2 media capacity

System Element

- Composite vessel (Charging pressure, Media volumetrics)
- Powder densification (Media volumetrics, Powder loading, Expansion forces)
- Oil HT fluid (Water reactivity)

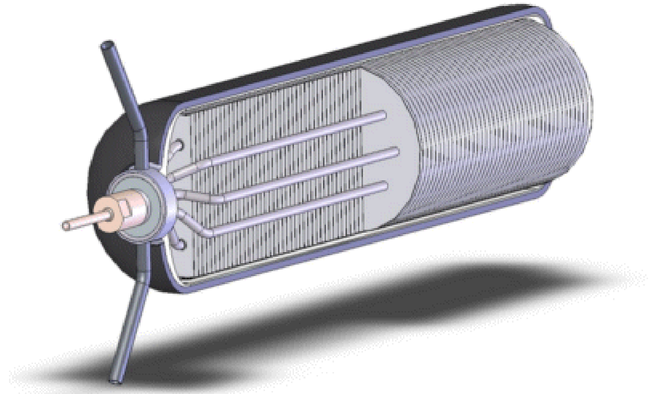
$NaAlH_4$ Prototypes

1



Full scale – 19 kg hydride
Aluminum foam

2



Sub scale – 3.5 kg hydride
Aluminum fins

Second Prototype Overview

Improvements over first prototype:

- Lighter weight composite vessel with conventional domed end.
- Lighter weight heat exchanger with fins for superior long range heat transport.
- Denser powder packing which is performed within a pre-constructed system, improving both volumetrics and gravimetrics.

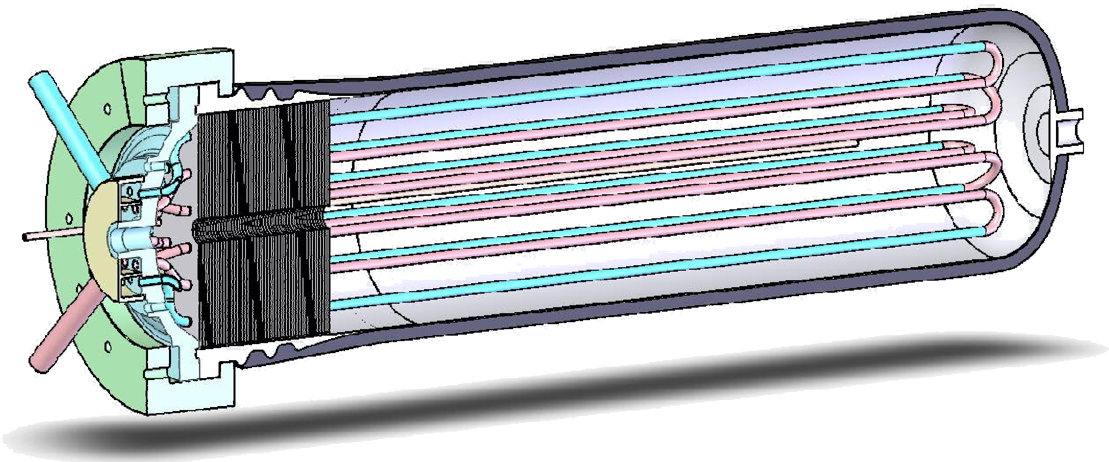
Characteristics of second prototype

- Developed at nominally $(1/2)^3 = 1/8^{th}$ scale or 1/8 kg H2.
- Intermediate size to balance:
  - Fabrication challenges – keep unique supporting hardware to reasonable size and cost.
  - Ability to demonstrate technologies and perform projections.

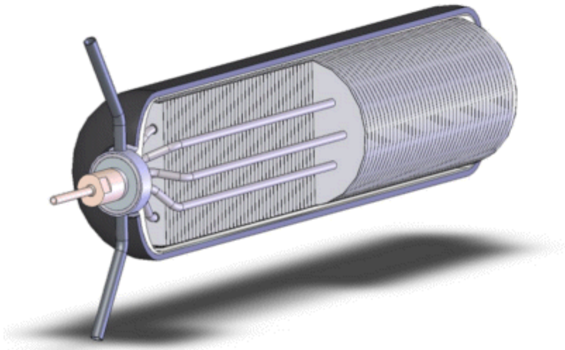
Prototype 2 Size Scale Replan

Modifying the plan to design, fabricate and test a $(1/2)^3 = 1/8^{th}$ scale system was the right thing to do.

- Greater emphasis of resources on powder densification and demonstration of lightweight, as-fabricated system.
- Lower degree of “projecting” to 2.3 wt% and 2.5 wt% systems.
- Recommend this size scale for first prototypes in future efforts.



Original, full scale plan
nominally 25 kg of hydride



Prototype 2
3.5 kg of hydride

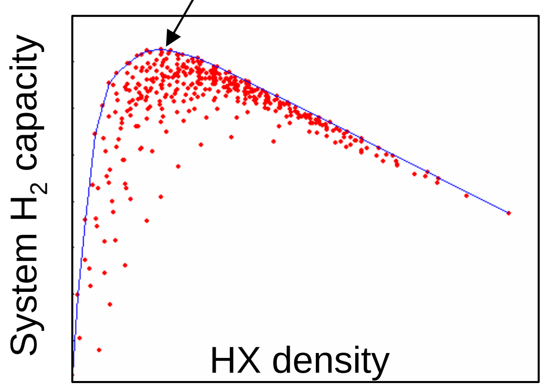
Prototype 2 Heat Exchanger Design

Fabricated heat exchanger based on the following design process:

Low Length Scale FEA

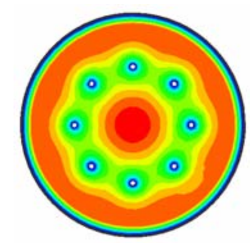
Fin unit cell

Optimize:
- Fin thickness
- Fin spacing
- Tubing OD
- Tubing spacing

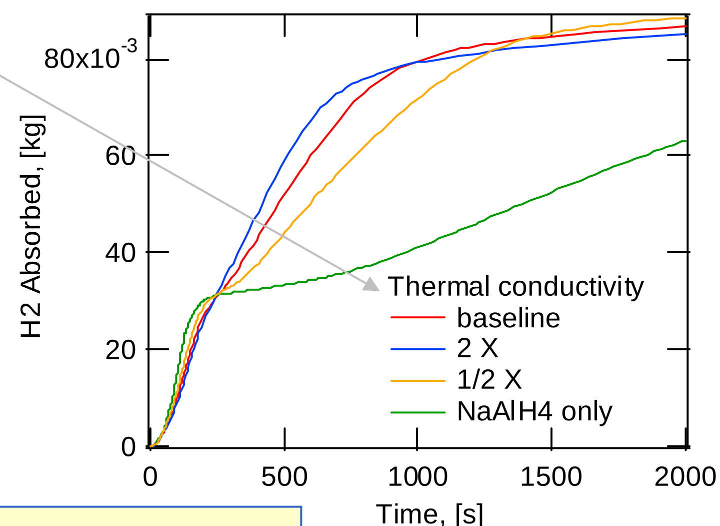


Larger Length Scale FEA

System cross section



Optimize:
- Tubing positioning



30% reduction in HX mass

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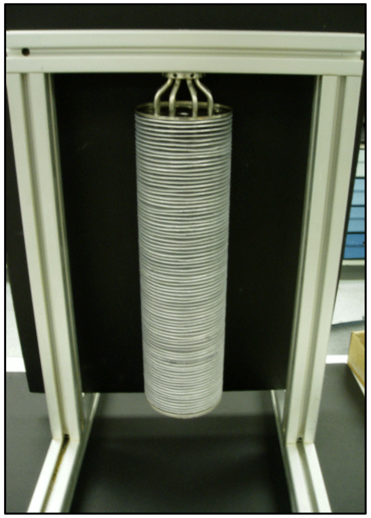
Fabrication

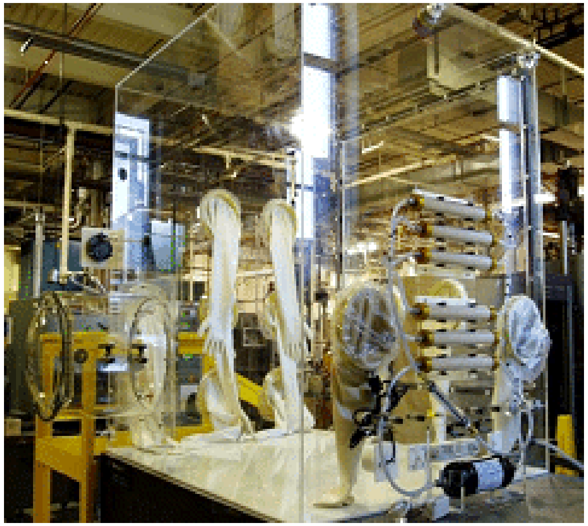
Finned Tube
Heat Exchanger



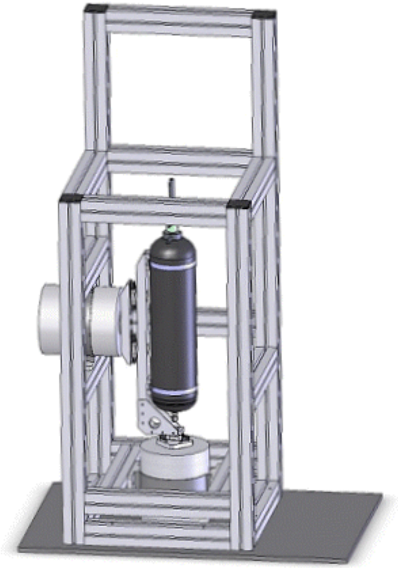
Stainless Steel Liner

Carbon Fiber / Epoxy
Overwrap

5’ x 5’ x 4’ Assembly
Glove Box



Shaker System



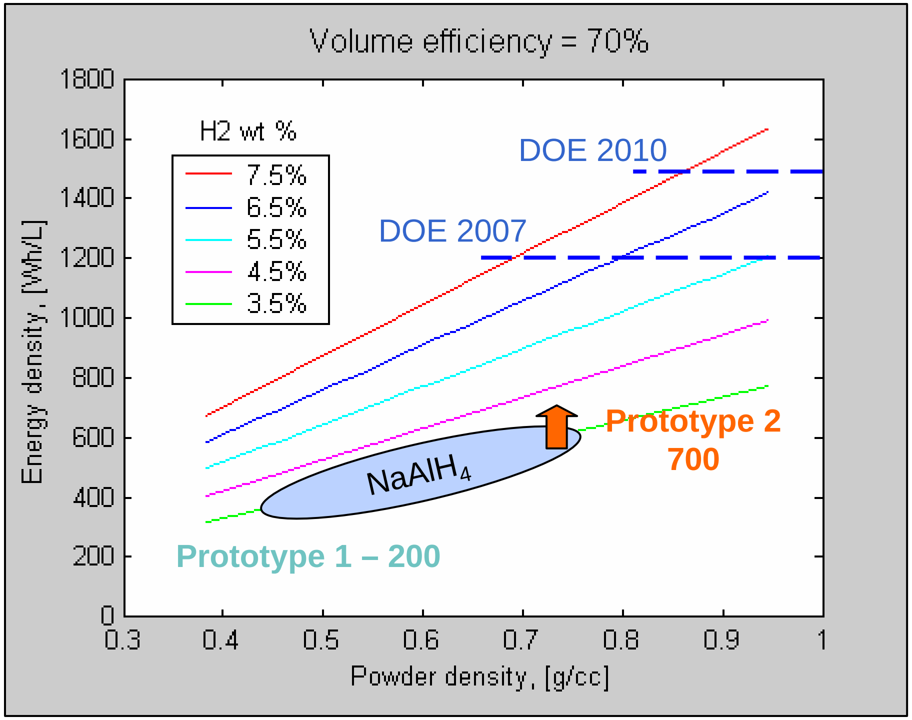
Storage Volumetrics Overview

Energy density is the product of

- *Hydride powder density*
- H_2 weight % capacity
- System volumetric efficiency

Prototype improvement

- Prototype 1: 200 Wh / L
- Prototype 2: 700 Wh / L

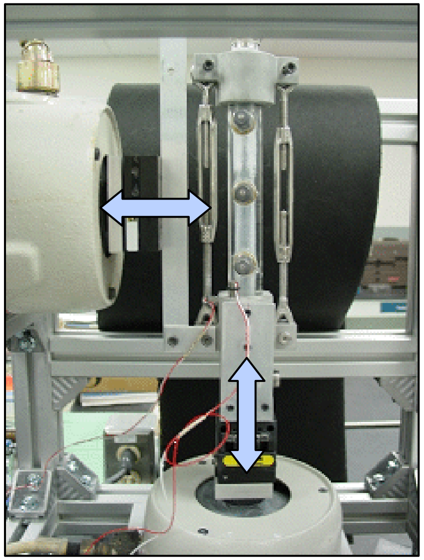


Hydride powder density is as important as H_2 weight % capacity for system volumetric capacity

Powder Loading – Procedure Development

Development of loading procedure

Results for second prototype hydride powder

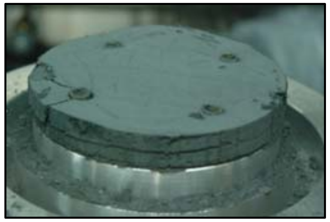


Dual axis vibratory shaker

Controlled amplitudes and frequencies

Powder column

0.72 +/- 0.02 g/cc



Disassembled finned test article

> 0.77 g/cc

Prototype 2

0.72 to 0.76 g/cc

Prototype 1

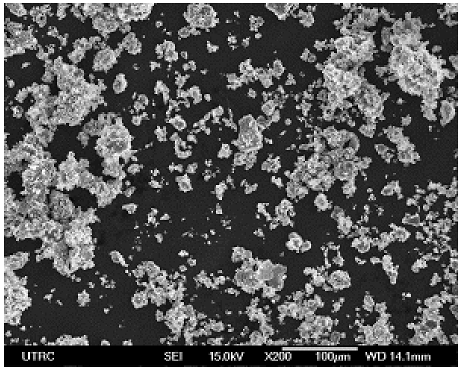
0.44 g/cc

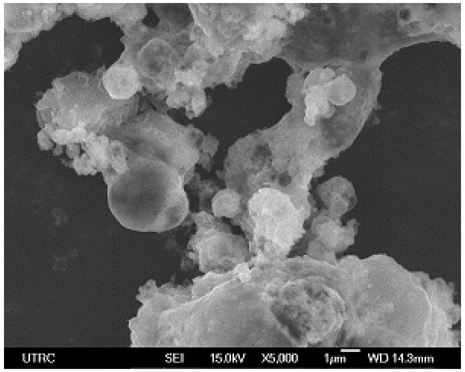
Consistent densities across multiple configurations & geometries

Milling and Densification (Powder Column)

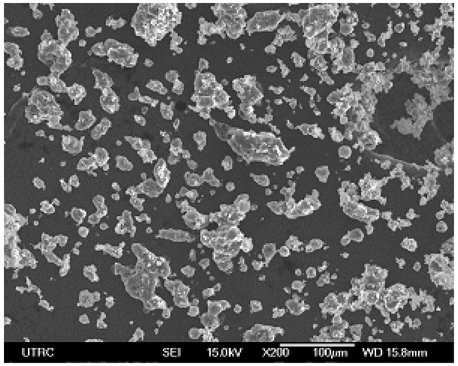
Ball milling procedures affect not only kinetics, but also powder densification.

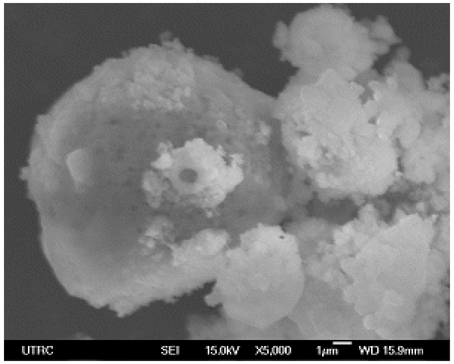
0.64 g/cc





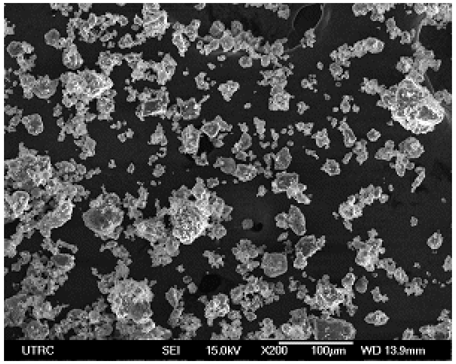
0.85 g/cc

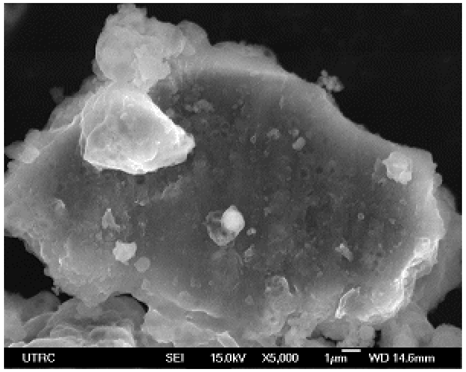




Used for projection

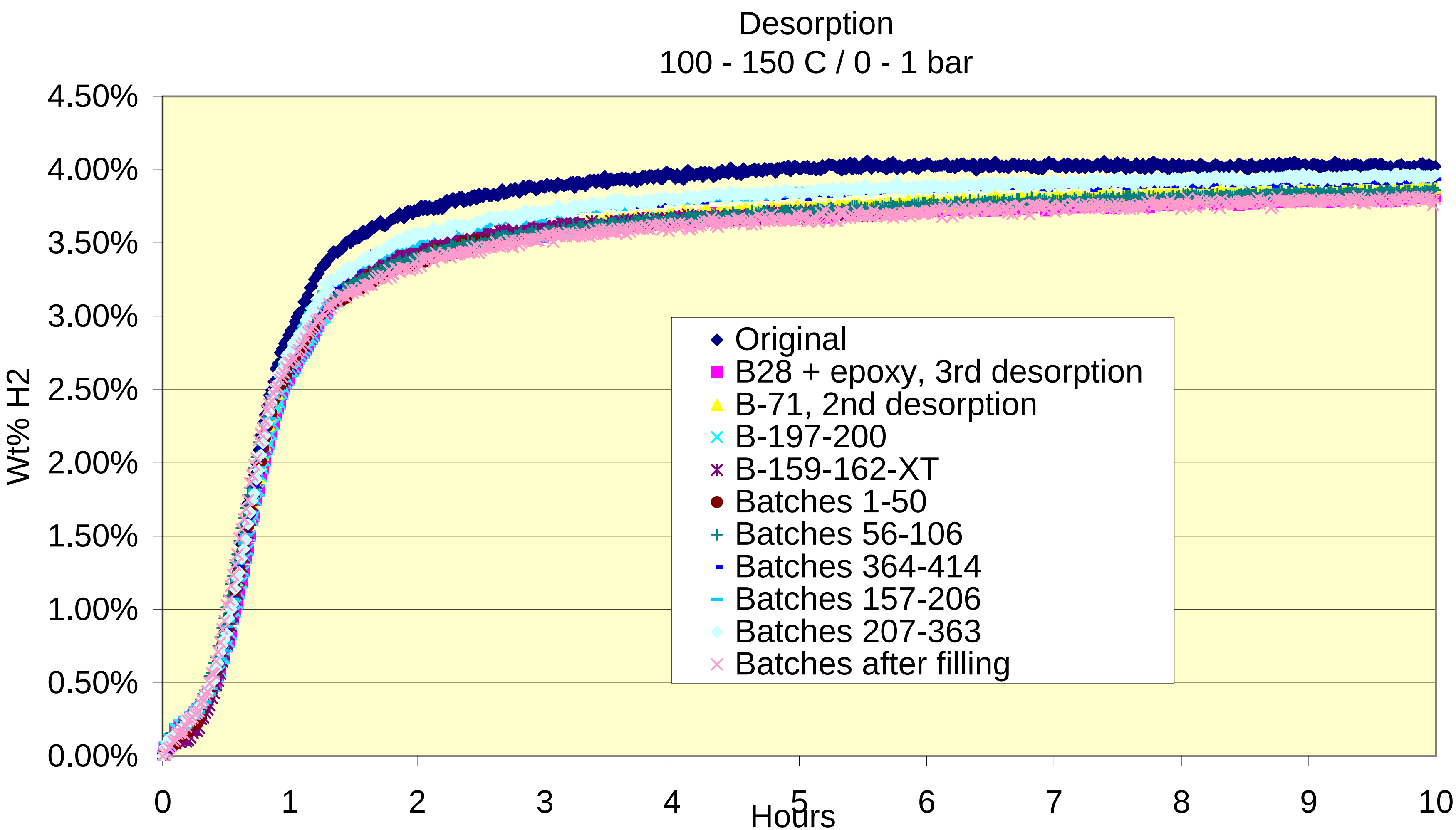
0.72 g/cc





Prototype 2 material

Material Quality Assurance – Batch Testing



At desorption temperatures ramping from 100 to 150 C, capacity is nominally 3.5 to 3.7 wt%

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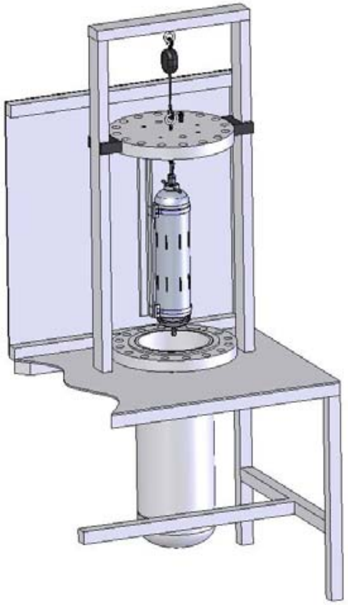
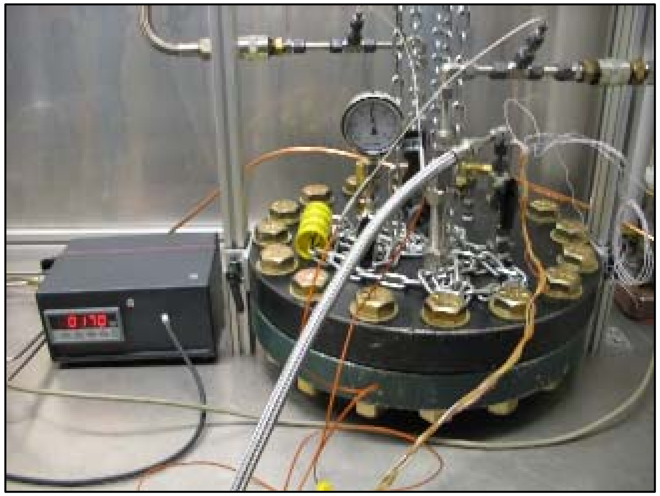
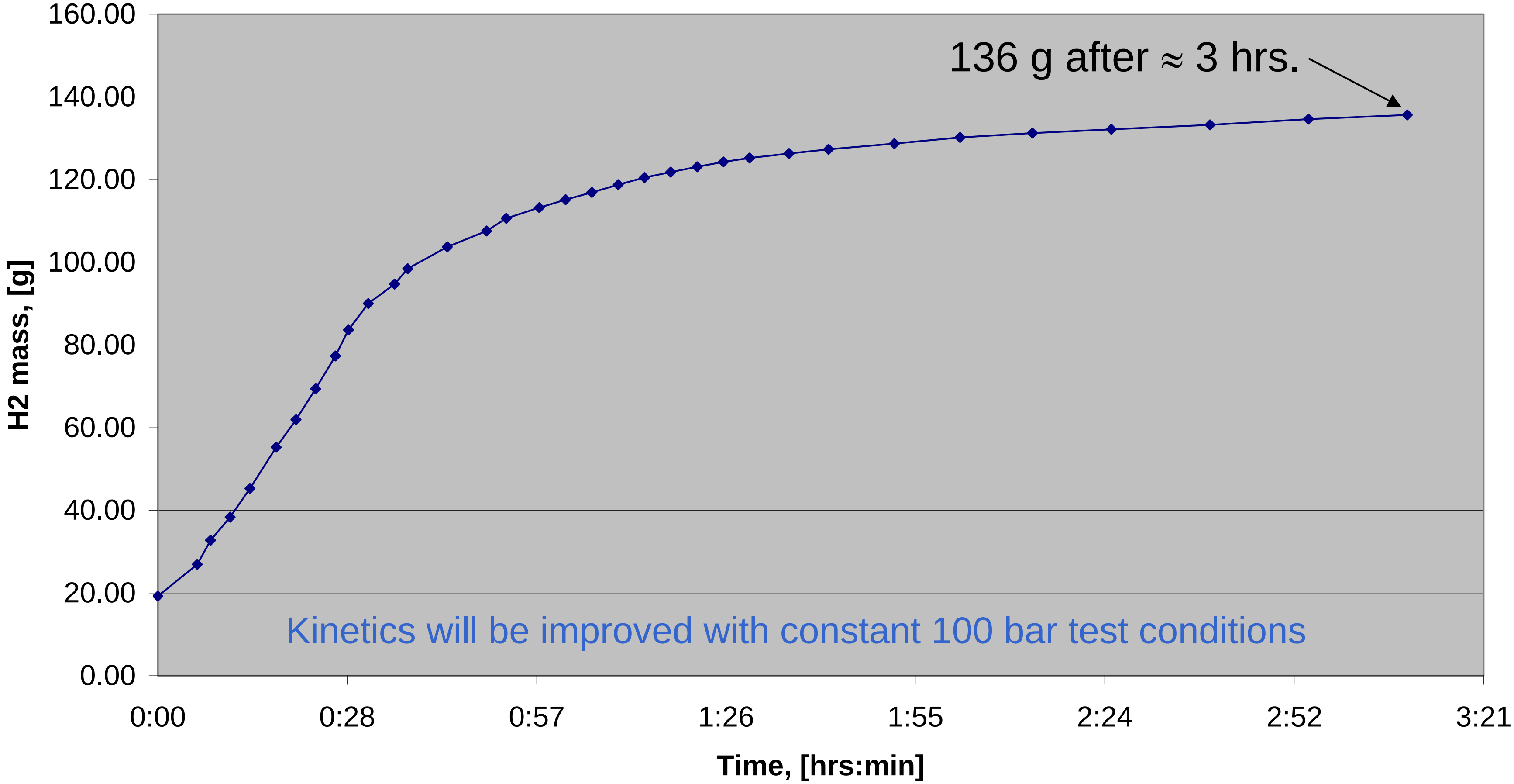
Prototype 2 Testing Apparatus

- Addition of secondary vessel for risk reduction
- First test – modified Sievert's apparatus approach with 100 bar dosing





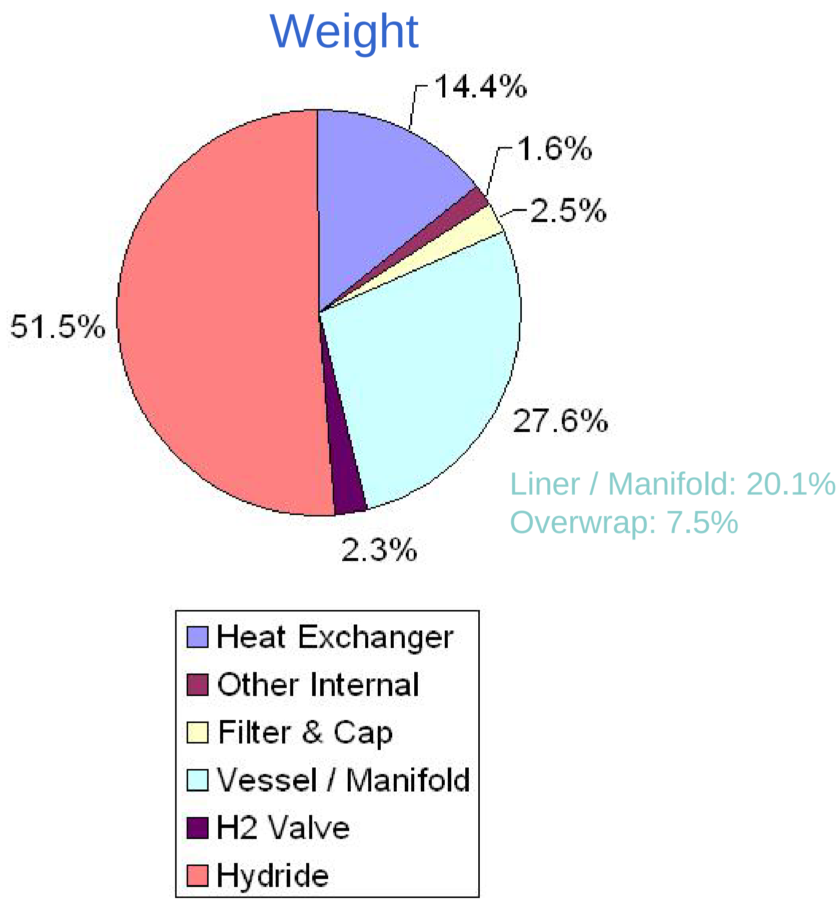
Absorption Test

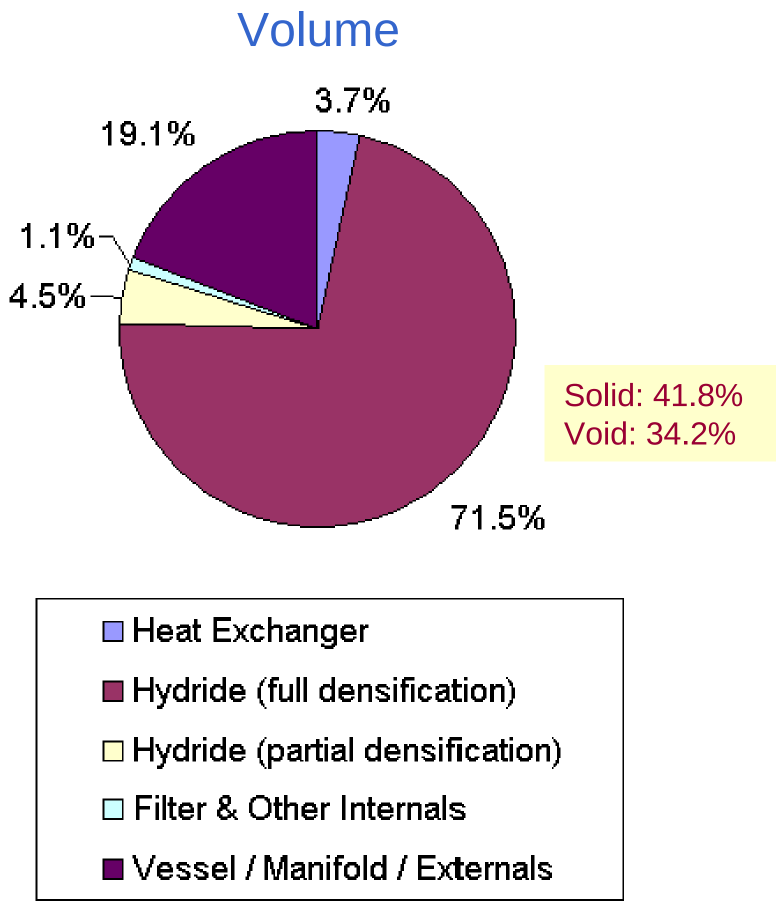


- Hydrogen was added to the prototype in doses from an accumulator volume.
- System charging pressure is reduced from its starting value of ≈ 100 bar after dosing.
- The first point includes both compressed gas and absorbed hydrogen storage.
- Desorption: 150 C & ≈ 1 atm.

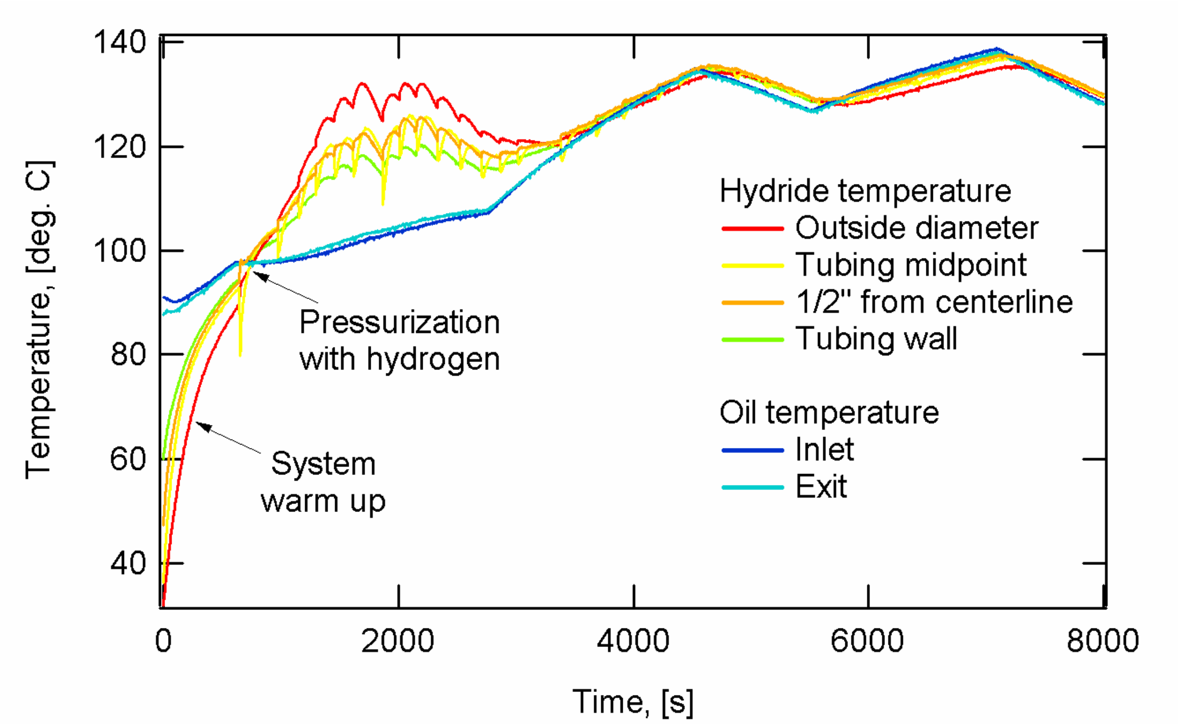
Weight and Volume

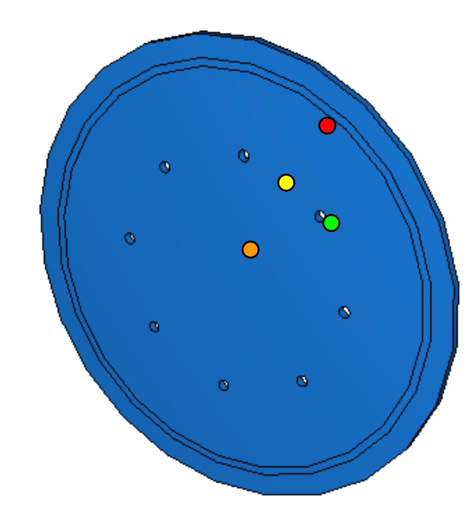
- Hydride material: 3.5 kg, 0.72 g/cc
- Gravimetric capacity = 136 / 6846 = 0.020 (g H2 / g System)
- Volumetric capacity = 136 / 6450 = 0.021 (g / cc)





Absorption Test – Temperatures





- Four internal thermocouples located at ¼ length and as given in the figure.
- Sheathed type K with 0.032” diameter– some averaging ⟶ 
- Apparent exothermic reaction for slightly less than 1 hr.
- Pressure data only at dosing points, not continuous.
- Detailed model comparisons will be made with subsequent data.

Testing Status

Modifications and Issues:

- Improvements in oil temperature management.
- Significant noise in pressure transducer data was reduced.
- Addition of Coriollis force flow meter – will use burst flow to improve accuracy.
- After being dormant for almost 2 months, a leak has occurred:
  - Pressurization to 1420 psi was normal, 1510 psi resulted in rapid leak rate.
  - Due to possible ejection of powder into secondary containment vessel, our neutralization process was applied before removing the lid. Upon opening secondary vessel, no ejected powder was noted.
  - The system was leaked check with helium and the source confirmed to be the O-ring. A metal-to-metal seal was used to keep the Viton O-ring from being exposed to hydride which did not perform as expected. A Kalrez O-ring is now being installed.

System Scaling and Projection

Elements of preliminary projection:

- Potential hydride mass = 0.85 g/cc * 4900 cc = 4165 g for subscale
- Scaling vessel to full size (10X)
  - Liner retains 0.020” thickness; liner mass scales as (Volume)^(2/3)
  - Hydrogen valve has the same mass
- Resulting full scale gravimetric efficiency is 0.63 (kg hydride / kg system)
- At 0.85 g/cc, 140 C and 100 bar, the compressed gas storage is effectively 0.25 wt% (kg H2 gas / kg hydride).
- With a 3.4 wt% material, system would be

$$(3.4\% + 0.25\%) * 0.63 = 2.3\%$$

All of these projection elements have been demonstrated separately, substantiating that such a 2.3 wt% system could be constructed with the currently developed technology.

Performance Metrics and Projections

Complex Compound Hydride Storage System (CCHSS) Performance Metrics

Characteristics & Metrics	Units	$NaAlH_4$ Prototype 2	$NaAlH_4$ Projected	TBD hydride	TBD hydride	DOE Targets 2007	DOE Targets 2010
Material & Version:		$NaAlH_4$ Prototype 2	$NaAlH_4$ Projected	TBD hydride	TBD hydride		
Material gravimetric capacity	*% kg H_2 / kg hydride*	3.4%	3.4% → d	6.5% → d	8.0%		
H_2 charging pressure	bar	100	100	70	50		
Packed powder density	*kg hydride / m^3 powder*	720 → b	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 → c	0.63 → e	0.67 → e	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%**
	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**
	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

Need 8 wt% material and 75% mass efficiency of system to meet 6 wt% system

Evaluation of New Materials – System Integration

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

Powder column densification rig

* Densification of as-received new materials, with no further processing.
** 6% TiF_3-$NaAlH_4$, dehydrided, and paint shaken, close to "as-received."

Use of systems development methods to evaluate novel materials.

Conclusions

Second prototype system development resulted in significant gravimetric and volumetric improvements:

		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 H2 / kg sys.*	0.4%	2.0%	1.7%	2.3%
Powder density	*g / cc*	0.44	0.72	0.60	0.85
Volumetric density	*kWh / L*	0.20	0.70	0.60	0.80