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

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STP 1

Overview

- **Timeline**
  - 4/1/02 Start
  - 9/30/06 End
  - 85% Complete
- **Budget**
  - $3.8M Total Program
    - $2.7M DOE
    - $1.1M (28%) UTC
  - $0.8M DOE FY05
  - $0.8M DOE FY06
- **Barriers Addressed**
  - System Gravimetric Capacity: 2 kWh/kg
  - System Volumetric Capacity: 1.5 kWh/L
  - Charging Rate: 1.5 kg H_2/min
  - Safety
- **Partners**
  - UTC Fuel Cells
  - University of Hawaii
  - Hydrogen Components, Inc. (HCI)
  - QuesTek, LLC
  - Albemarle Corporation
  - Spencer Composites
  - Lyons Tool & Die

Objectives

Project Objectives

- Design, fabricate and evaluate prototype solid state hydrogen storage systems based on catalyzed $NaAlH_4$ which can be used with other reversible complex hydrides of similar thermodynamics with minimal redesign.
- Identify and address key challenges for materials and systems, particularly those which differ from conventional metal hydrides.

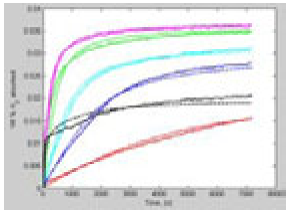
Past Year Objectives

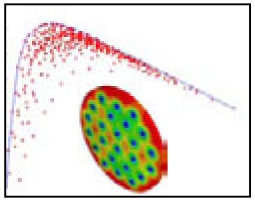
- Prototype 1: Evaluation
    - Test method refinement
    - Absorption / desorption experiments
    - Model verification
- Prototype 2: Development
    - Scaled-up media processing & catalysis
    - Optimized finned tube heat exchanger design
    - Powder densification development

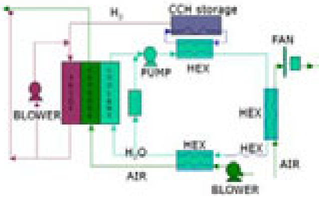
Approach

Apply modeling, sub-scale experimentation and full scale development to identify & address critical technologies for complex hydride systems:

- Safety Analysis
- Media Kinetic Experiments & Modeling
- Heat Transfer Analysis & Optimization
- 50 g H_2 Subscale Experiments
- Full Scale Prototype 1
  - Component design & fabrication
  - Assembly hardware
  - Evaluation facility
- Prototype 2
  - Address identified challenges
- Fuel Cell Integration Analysis





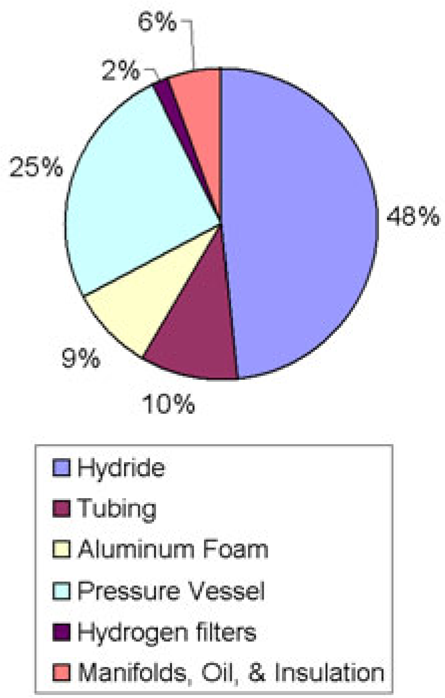


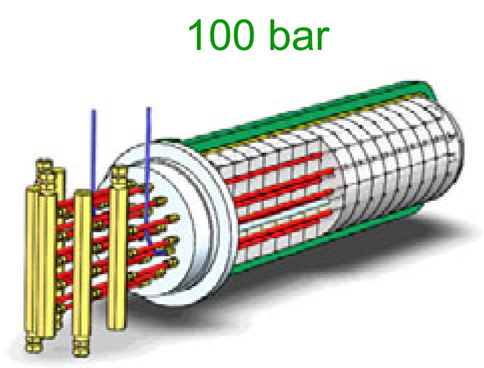
Prototype 1 Overview

Prototype 1 elements

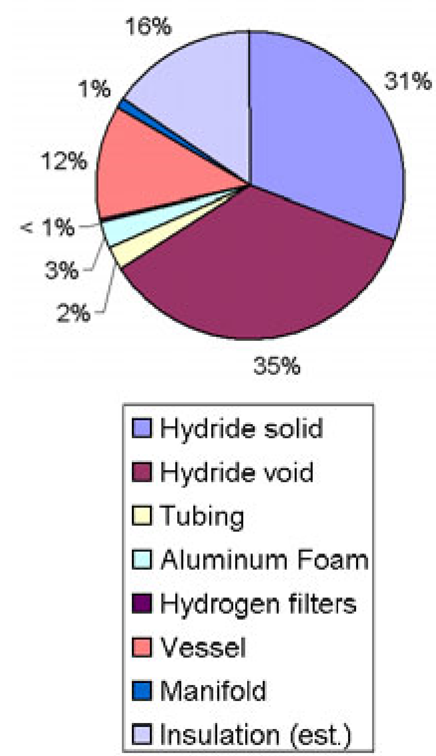
- High temperature (250 C) composite vessel
- Optimized aluminum foam based heat exchanger
- Full scale fabrication & testing
- 19 kg of $NaAlH_4$

Adjusted mass fractions





Adjusted volume fractions



Full Scale Testing

Continued testing up to 25 cycles

Test Conditions

Charging

- Std. discharge: 150^{o}C/vac./16hrs.
- 70 and 100 bar charging (16 hrs):
    - 80 ^{o}C
    - 100 ^{o}C

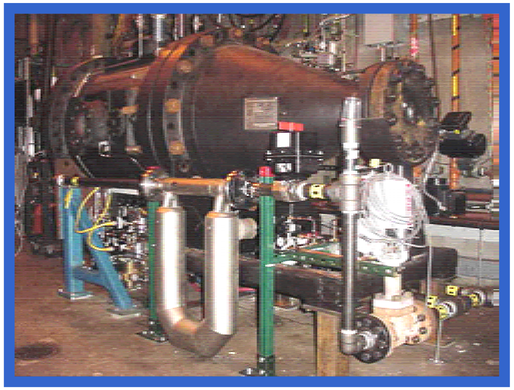
Discharging

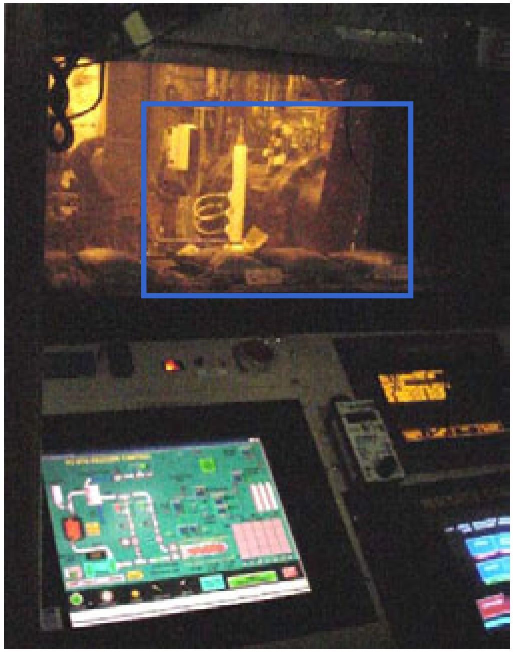
- Std. charge: 100^{o}C/100bar/16hr
- 2 bar discharging (16 hrs)
    - 90 ^{o}C
    - 100 ^{o}C

Data

- 2 ranges of Coriolis H_2 mass flow meters
- 2 vessel and 4 system pressure transducers
- 12 vessel & 15 system thermocouples
- 6 strain gauges

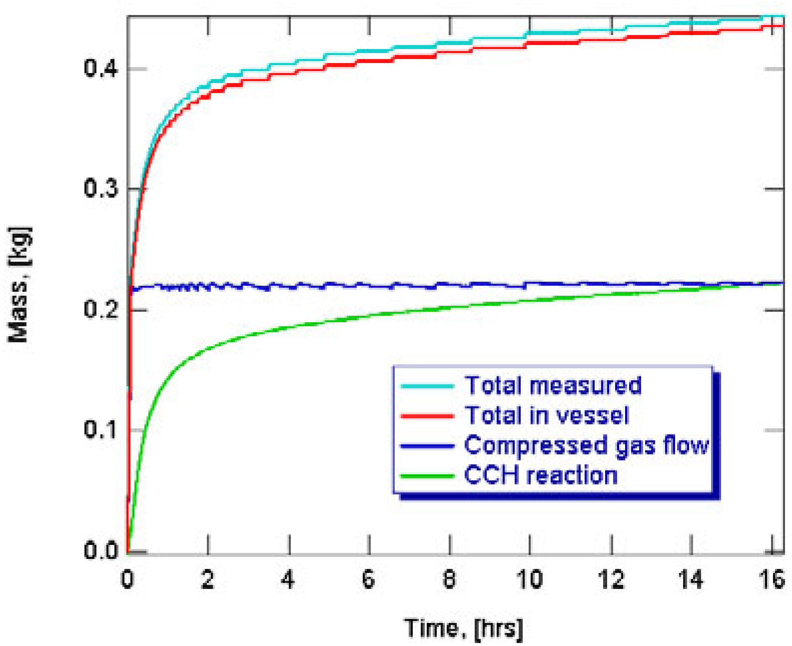
Test cell with isolated control

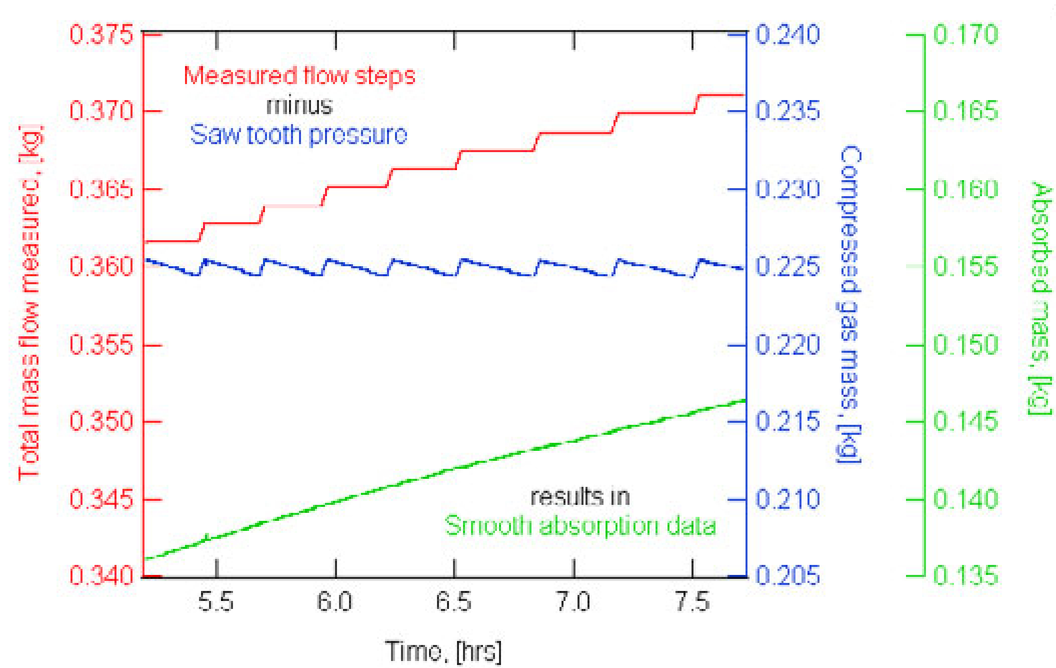




Test Methodology and Data

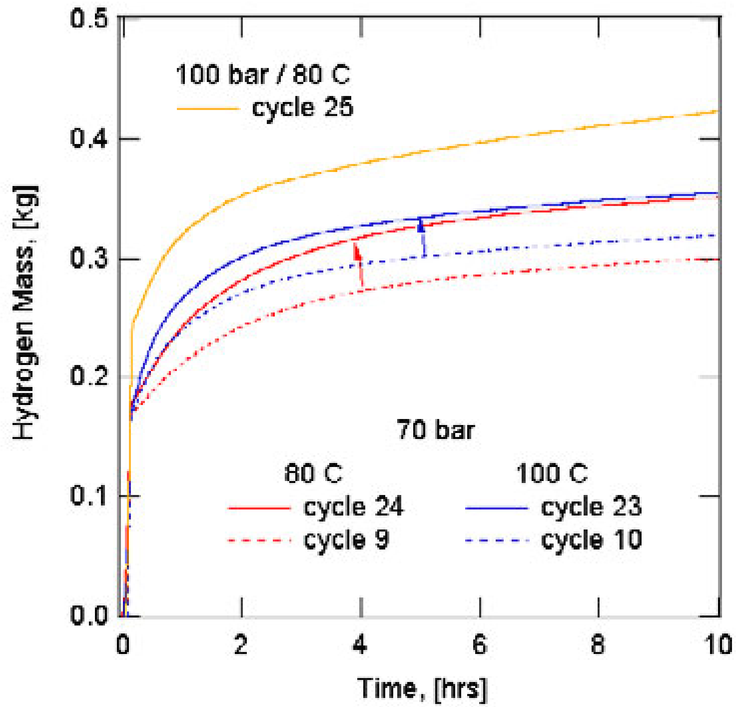
- Totalized mass flow and pressure measurements are used to calculate absorbed / desorbed mass curves.
- A burst flow mode was developed to increase the effective resolution of the mass flow meters.





Absorption Tests

- Ultimate capacity of system is nominally 1 lb. (0.45 kg) of H_2
- Cyclic improvement is apparent for both 80 and 100 C at 70 bar



Challenges identified from first prototype experience

- Material processing scale-up with low cost catalyst
- Powder densification compatible with system fabrication

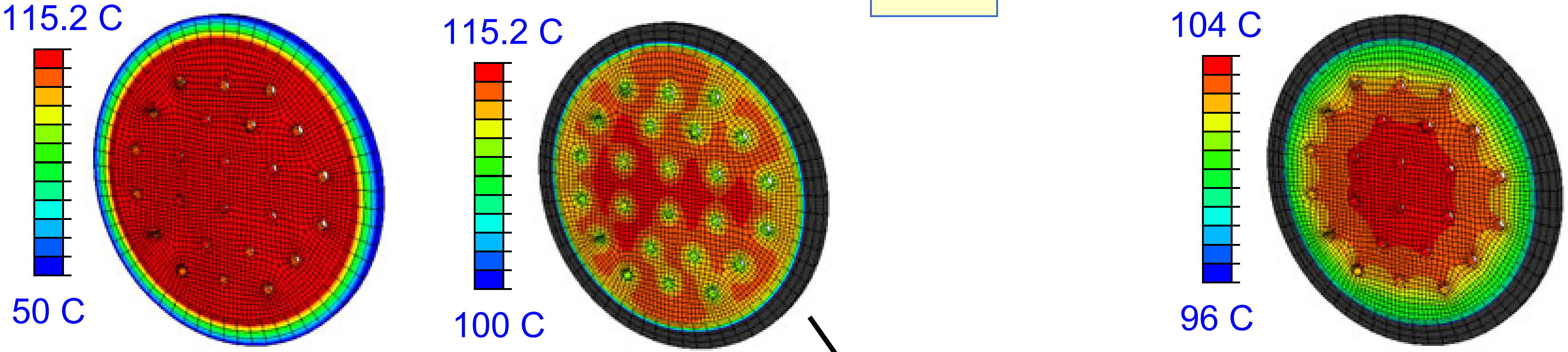
which have been addressed in second prototype development

Prototype 1 Model Comparison

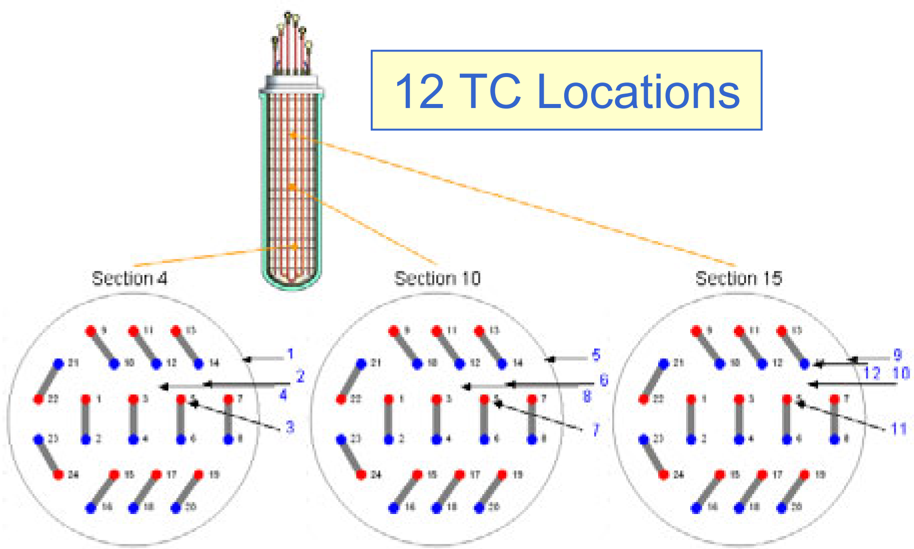
943 s (peak T)

FEA

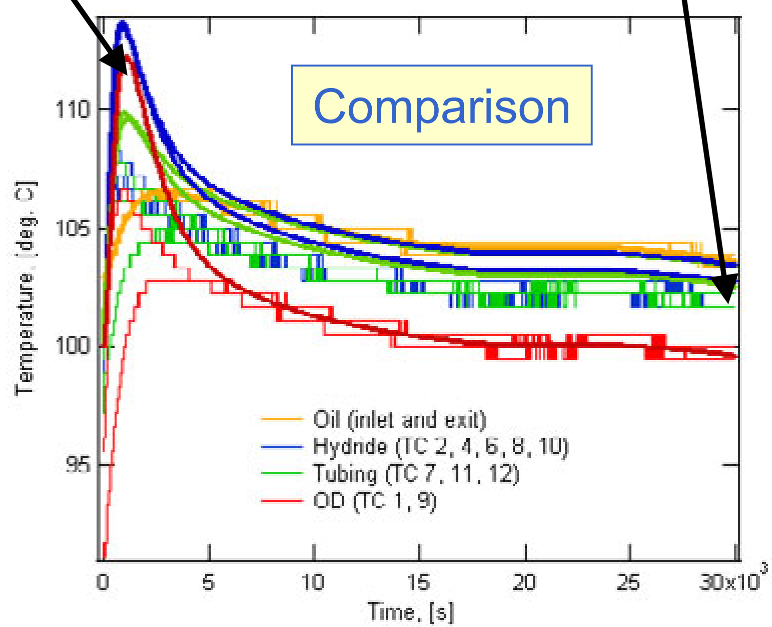
30,000 s



12 TC Locations



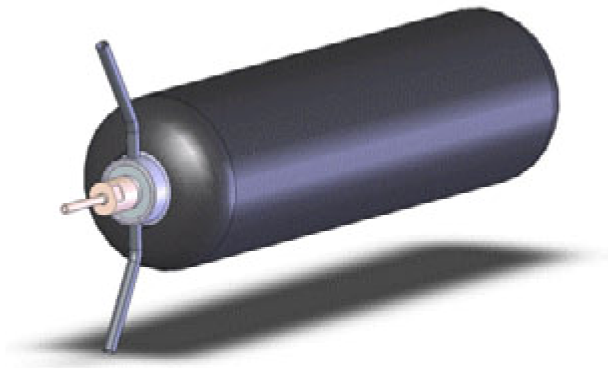
Comparison



Prototype 2 Overview

Past year activities

- Scaled-up media processing & catalysis
- Optimized finned tube heat exchanger design
- Powder densification development
- Compact oil manifold



Catalysis Experiments

Materials

Commercial purity $NaAlH_4$: 87 % $NaAlH_4$, 5 % Na_3AlH_6, 7 % Al, 1 % inerts

$TiCl_3$ Costs
- 2001 - $154/m Ti^{+3}
- 2002 - $924/m Ti^{+3}
- 2005 - $1,955/m Ti^{+3}

Alternate Catalysts (2005)
- $TiCl_2$ - $1,452/m Ti^{+2}
- TiF_4 - $157/m Ti^{+4}
- TiF_3 - $233/m Ti^{+3}
- $TiCl_3$*1/3$AlCl_3$ - $46/m Ti^{+3}

Compositions Examined
- 6% $TiCl_3$
- 4% $TiCl_3$
- 4% $CeCl_3$
- 6% TiF_3
- 3% $TiCl_3$*1/3$AlCl_3$

PCI Experimental Conditions

Isobaric Absorption
- 150°C/vac/24hrs
- T = 80, 100, 120 & 140 °C
- P = 68 bar

Isobaric Desorption
- 120°C/68bar/16hrs
- T = 70, 80, 90, 100, 110 & 120 °C
- P = 1 bar

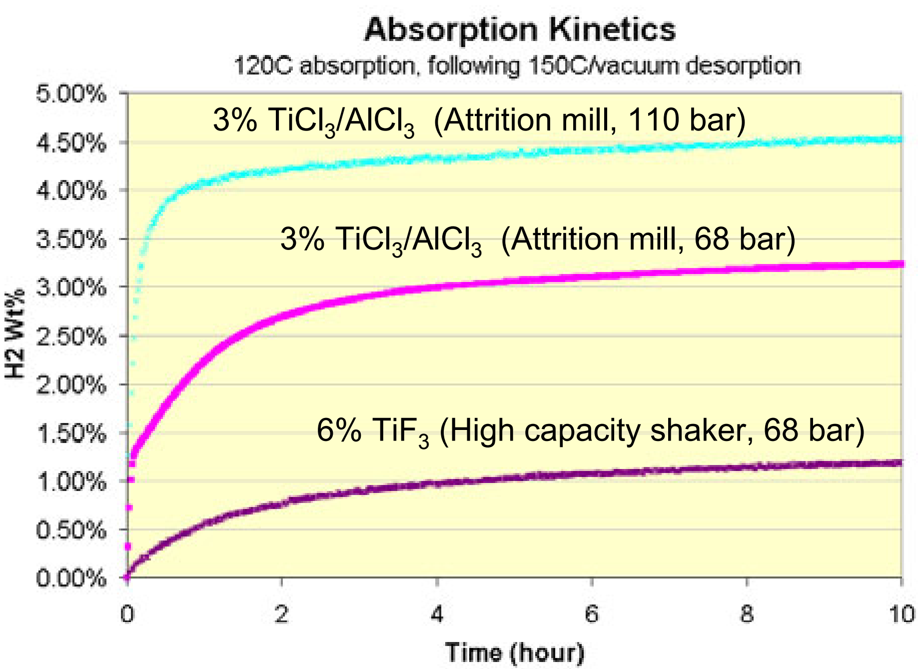
Isothermal Absorption
- 150°C/vac/24hrs
- T = 120 °C
- P = 50, 68, 90, 110 bar

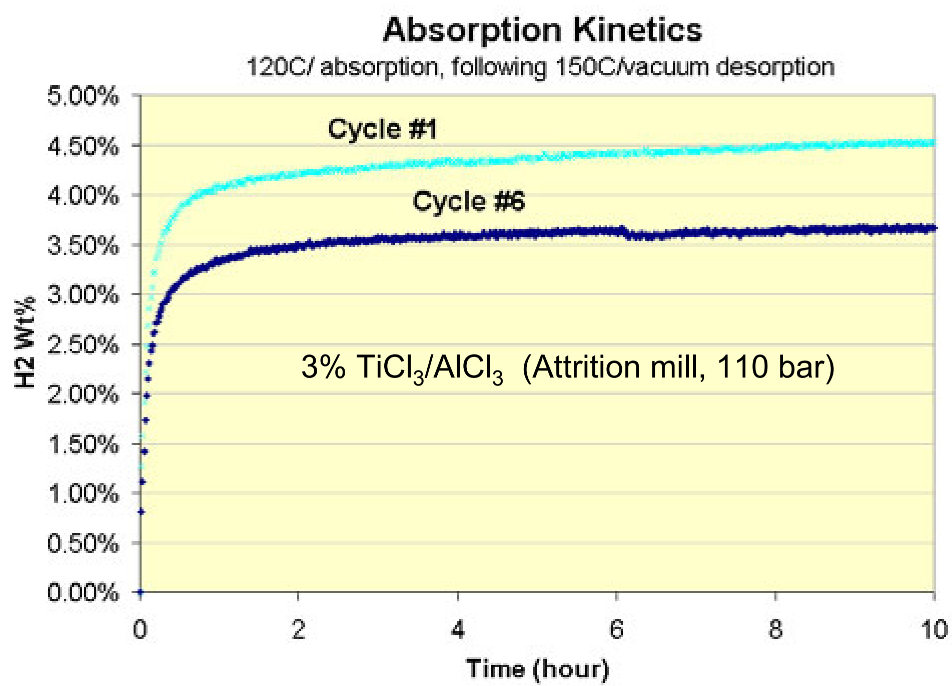
Processing Methods

- SPEX mill
  - 5 grams
  - 40 g / 16 Hz
- Tumble mill
  - 0.5 kg
  - 1 g / 1 Hz
- High capacity shaker
  - 0.5 kg
  - 15 g / 10 Hz
- Attrition mill
  - kg quantities
  - 60 – 350 RPM

Scaled-up Processing

Large scale processing
68 & 110 bar charging pressures





Large scale processing with a low cost catalyst results in effective capacities for $NaAlH_4$ between 3.2% and 3.5% after cycling.

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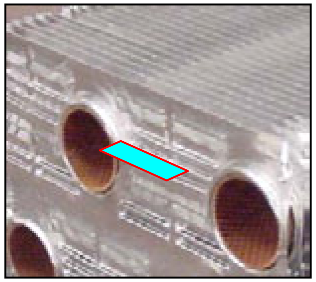
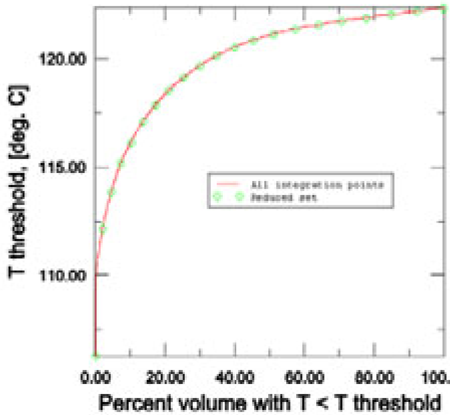
Heat Exchanger Design

(Air conditioner HX)



Unit cell FEA

T distribution



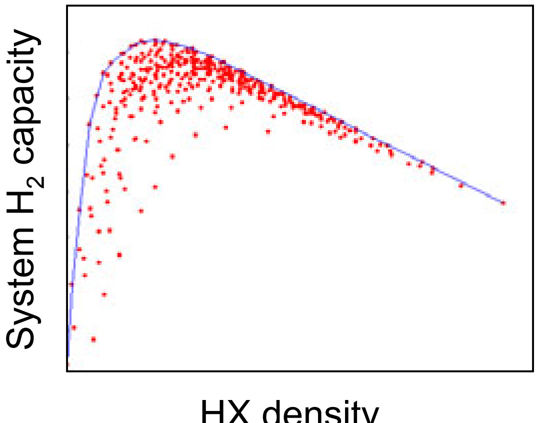
Design variables:
- Fin thickness
- Fin spacing
- Tubing OD
- Tubing spacing

Heat exchanger design and optimization based on a single fin unit cell and variable properties to estimate performance of the entire system

30% reduction in HX mass

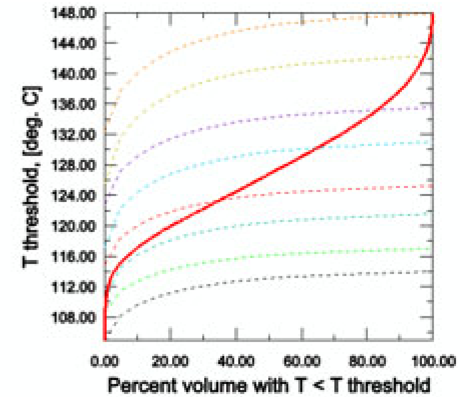
HX optimization

> 3000 simulations



Cell-to-cell variability

ex. thermal contact resistance



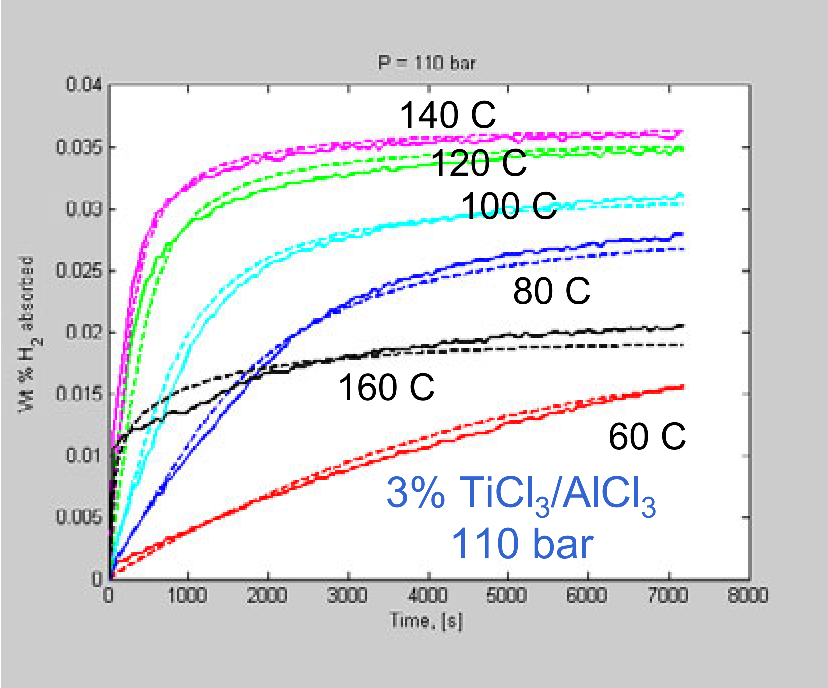
Reaction Kinetics Model

Recalibration for attrition milled 3% TiCl3 / AlCl3 material

$$\underset{C_1}{NaH + Al + 3/2\,H_2} \;\overset{r_1}{\leftrightarrow}{}^{r_2}\; \underset{C_2}{1/3\,Na_3AlH_6 + 2/3\,Al + H_2} \;\overset{r_3}{\leftrightarrow}{}^{r_4}\; \underset{C_3}{NaAlH_4}$$

$$\left(\frac{dC_2}{dt}\right)_{r2} = A_2 \exp\left(-\frac{E_2}{RT}\right) * \left(\frac{P_{e,2} - P}{P_{e,2}}\right) * \left(C_1 - C_1^{sat}(T)\right)^{\chi_2}$$

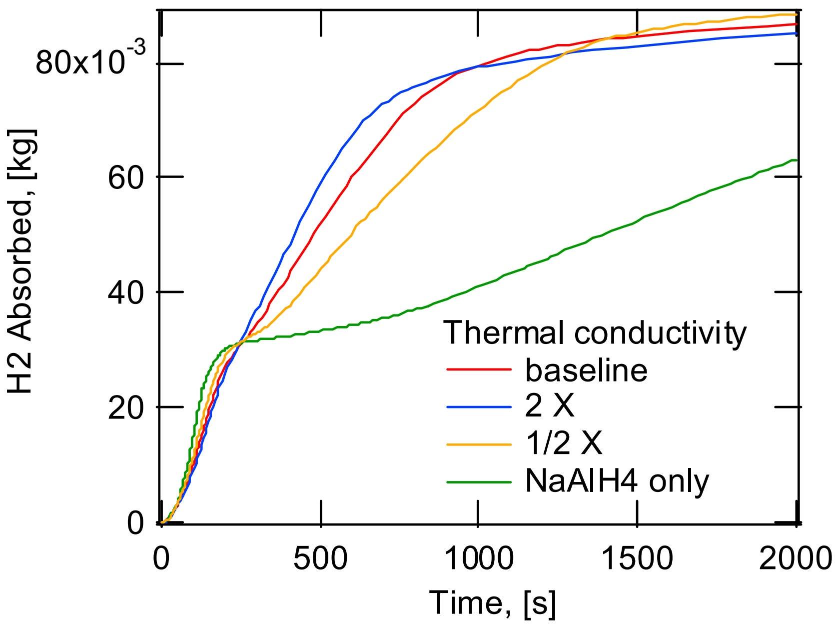
H_2 absorption: model vs. experiment



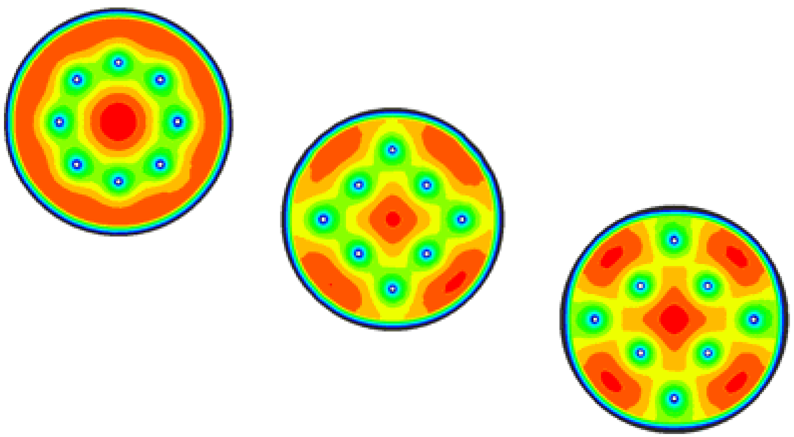
Heat Exchanger Design

Conduct higher length scale simulations of vessel cross section using effective properties determined from lower length scale fin unit cell simulations

Effective thermal conductivity



Maximum T uniformity & kinetics



Different tubing placements in vessel cross-section can result in similar performance

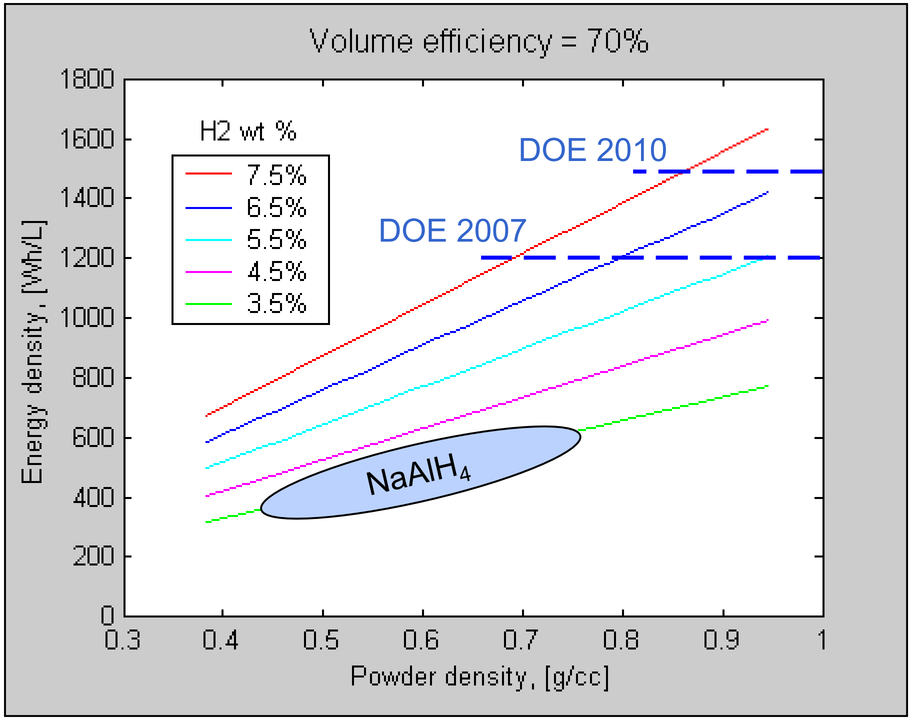
Optimal design developed which shows only minor improvement in absorption rate with increasing effective thermal conductivity (i.e. 2X fin mass).

Powder Densification Overview

Combination of

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

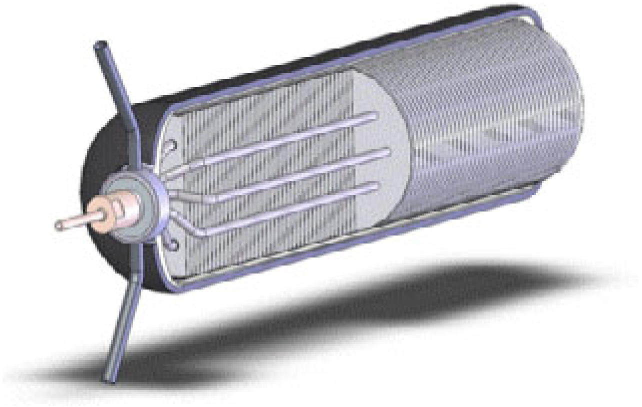
determine energy density



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

Powder Densification Approach

- Densification approach must be compatible with prototype fabrication method: composite vessel elevated T curing and $NaAlH_4$ safety concerns ⇒ fabricate composite vessel before powder loading.
- Goal to have lightest weight heat exchanger and pressure vessel ⇒ construct optimized finned tube heat exchanger within conventional dual domed vessel, requiring hydride powder loading through a reduced size port.

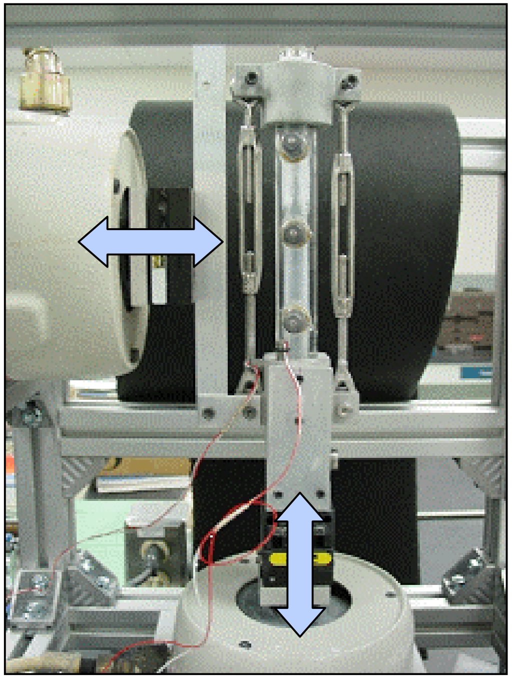


$NaAlH_4$ and other lightweight complex hydrides are considerably more difficult to pack than conventional metal hydrides ($LaNi_5$).

Creates challenge to densely load $NaAlH_4$ within the HX structure through a small port.

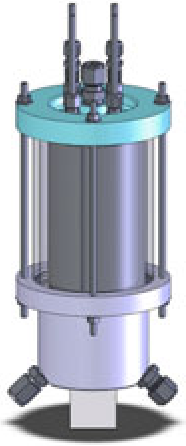
Powder Densification Experiments

Develop powder loading procedure with a versatile, instrumented vibratory apparatus and progression of experimental configurations.

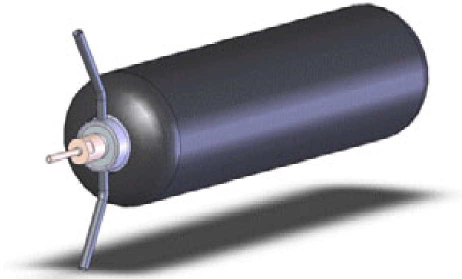


Dual axis vibratory shaker
Controlled amplitudes and frequencies

Powder column
Fundamental studies



Finned test article
Capable of disassembly

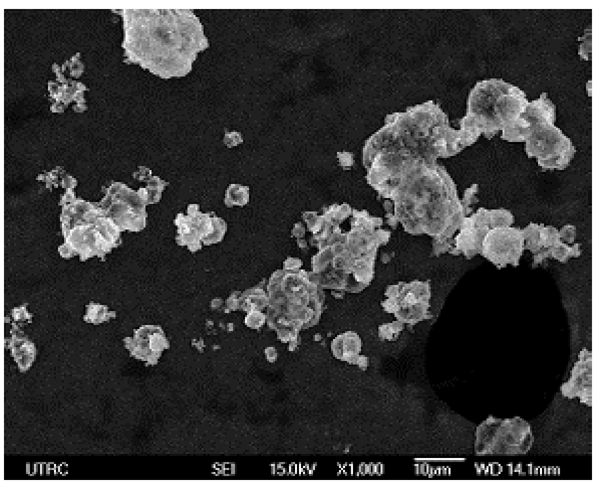


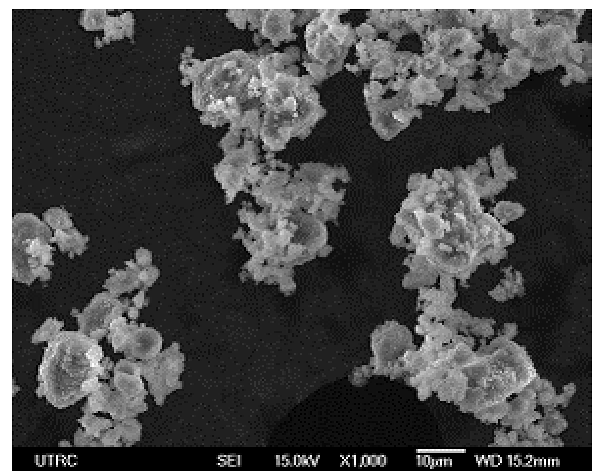
Prototype 2
Demonstration

$NaAlH_4$ Material States

Powder Bulk Densities, [g/cc]

	Process 1	Process 2	Process 3		
	As-received	As-received	As-received	Dehydrided	Recharged
Original	0.462	0.391	0.334	0.362	0.351
Vibratory settling	0.740	0.465	0.399	0.460	0.430
Enhanced settling	0.751	0.669	0.629	0.607	0.555

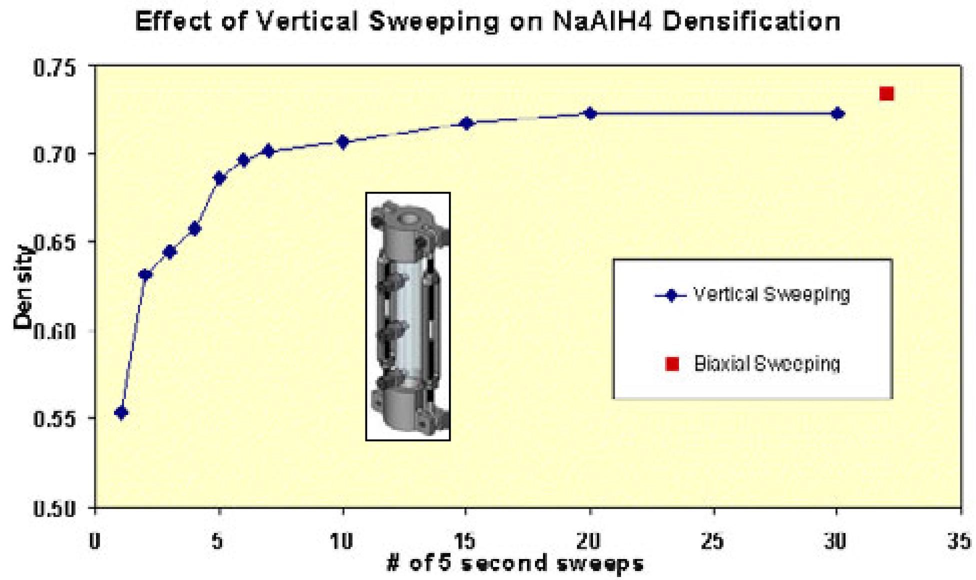




Material processing and compositional state have a significant influence on particle morphology and densification.

Powder Densification Results

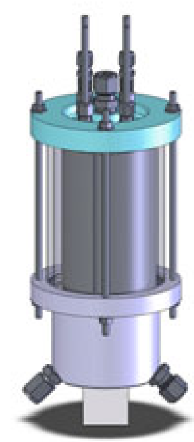
Enhancement methods developed in addition to baseline vibratory settling

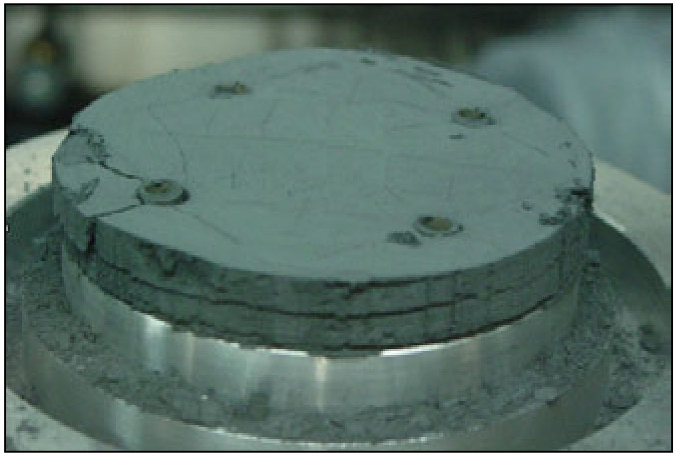


Average densities obtained

- Powder column: 0.75 g/cc
- Finned HX: 0.65 g/cc

Improvement over Prototype 1 actual average density of 0.44 g/cc and peak density of 0.6 g/cc





Future Work

- Conduct continued safety studies including decommissioning of Prototype 1.
- Fabricate Prototype 2 components and assemble.
- Test Prototype 2 – 9/30/06 Milestone.
- Compare system performance of Prototype 2 with modeling.
- Project material and system requirements to meet performance goals of 2.5 wt% and 4.5 wt% systems.
- Conclude contract with final report.

Summary

- First full scale $NaAlH_4$ prototype has been designed, fabricated and tested to identify and reprioritize key and in some cases unanticipated challenges (powder densification).
- Large scale processing method demonstrated with low cost catalyst having cyclic capacities up to 3.5 wt%.
- Finned tube heat exchanger designed with approximately 30% weight reduction.
- Powder loading and densification process developed compatible with composite vessel manufacture which has achieved densities between 0.65 and 0.75 g/cc.

Requirement	Units	DOE 2007 Targets	Prototype 1 Adjusted	Prototype 2 Projected
Gravimetric Density	kWh/kg kg H_2/kg	1.5 0.045	0.27 0.008	0.67 to 0.77 0.020 to 0.023
Volumetric Density	kWh/L kg H_2/L	1.2 0.036	0.18 0.0054	0.50 to 0.60 0.015 to 0.018

Supplemental Slides Not Required