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

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Merit Review
Philadelphia, PA
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Rev. B

Objective

To assist DoE in the development of an in-situ rechargeable hydrogen storage media and systems technologies for automotive transportation applications.

- Develop an engineering data base for catalyzed $NaAlH_4$ materials.
- Develop an understanding of the safety testing protocols and engineering design requirements for utilizing alanate materials.
- Develop, scale-up, build, bench demonstrate **an *in-situ* rechargeable 1 kg system and deliver a 5 kg H_2 capacity hydrogen storage system** suitable for operation of a PEMFC powered mid-size auto application based.

Budget

Funding: $2.45M *(28% cost share)*

FY ’04: *$939,000*

Duration: 4 years

Start: May 1, 2002

Technical Barrier & Targets

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC GO/NoGo
	Capacity	*kg*		5	
H_2 Storage Density	Gravimetric	*kWh/kg*	1.5	2	1.00
	Volumetric	*kWh/l*	1.2	1.5	0.55
Cost	Total life cycle (15 yr/150k miles)	*$(03)/kWh*	6.00	4.00	
	Fuel (gasoline equivilent)	*$(01)*	3.0	1.3	
	Marginal Fuel Cost (Ref. $1/kWh for H_2)	*$(03)/kgH₂*	NA	1.5	
Operating Temperature	Min.	*°C*	0	-30	
	Max.	*°C*	50	50	
Cycle Life	Cycle Life (0.25-100%)	*N*	500	1000	
	Mean	*%*	N/A	90	
	Confidence	*%*	N/A	90	

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC GO/NoGo
Hydrogen Delivery	Max. H_2 Delivery Temp.	*°C*	100		
	Min. H_2 Delivery Temp.	*°C*	-20	-30	
	Min. Full Flow	*g H_2/sec.*	3.0	4.0	0.30
	FC Min. Pressure	*kPa/bar*	250/2.5	250/2.5	
	ICE Min. Pressure	*kPa/bar*	1000/10	3500/35	
	Purity	*% (dry)*	99.9	99.9	
Transient Response	0-90% 90-0%	*sec.*	0.5	0.5	
	start to full flow @20°C	*sec.*	4.0	0.5	
	start to full flow @-20°C	*sec.*	8.0	4.0	
	Refueling Rate	*kg H_2/min.*	0.5	1.5	0.30
	Loss of Useable H_2	*g/hr kg H_2*	1.0	0.1	
	Permeation & Leakage	*scc/hr*	*Federal enclosed-area safety standard*		
	Toxicity		*Meets or exceeds applicable standards*		
	Safety		*Meets or exceeds applicable standards*		

Approach

Design a low pressure hydrogen storage system 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. Characterize **$NaAlH_4$** both empirically and analytically to obtain the highest performance composition.

This is a challenge to the hydrogen storage community to develop a material superior to $NaAlH_4$ in (i) gravimetric capacity (ii) charging rate at $\leq$100bar & (iii) discharge rate at $\leq$90°C.

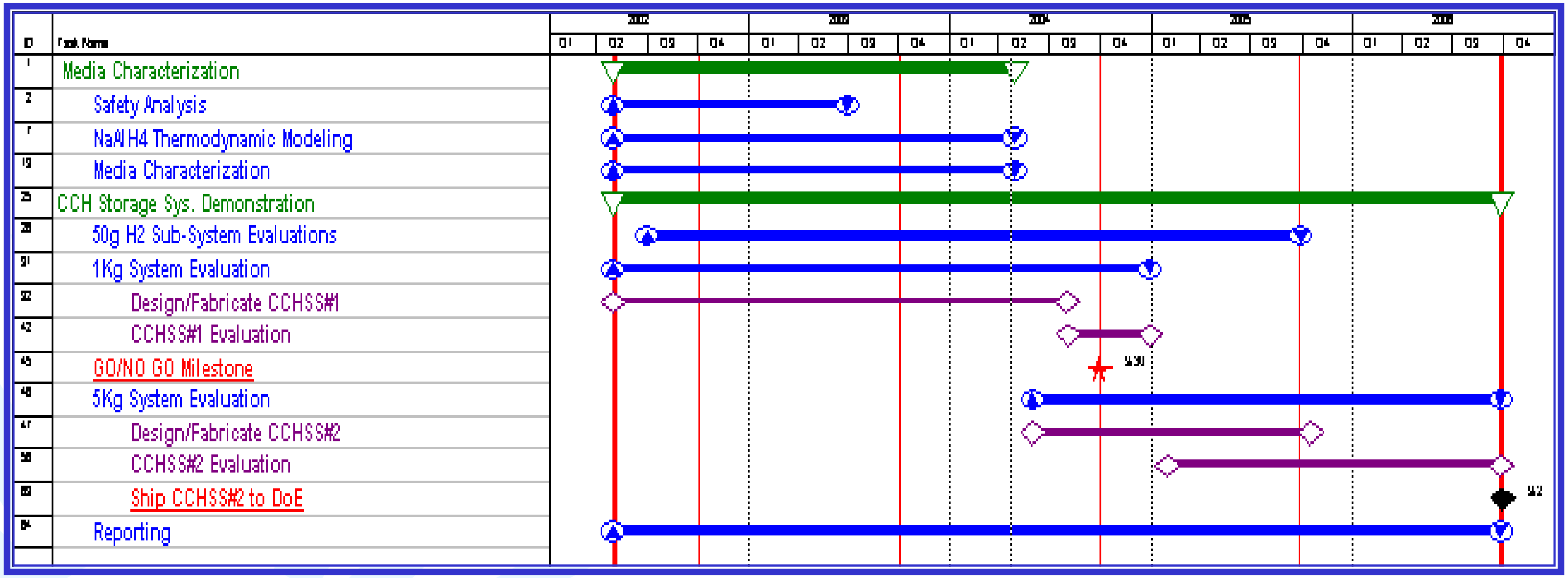
Safety

- Quantification of the safety risks associated with utilization of catalyzed $NaAlH_4$ materials.

- Identification of safety vulnerabilities and risk mitigation strategies in:
  - (i) testing laboratory quantities of $NaAlH_4$,
  - (ii) large scale production and handling of catalyzed NaAlH4 materials,
  - (iii) building and loading of a system utilizing up to 25 kg of catalyzed NaAlH4, and
  - (iv) building a testing system for evaluating the performance of an alanate hydrogen storage system with a 1 kg H_2 capacity.

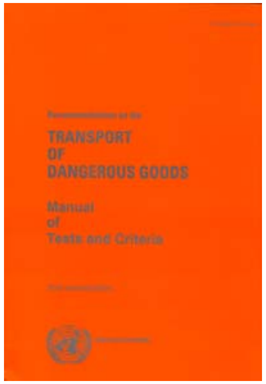
- Organizing IEA Task XVII break out session on alanate safety procedures & lessons learned.

Timeline



- **Phase I – Media Characterization**
  - – Safety Analysis
  - – Thermodynamic Modeling
  - – Media Characterization
    - Kinetics
    - Cyclic Stability
- **Phase II – System Demonstration**
  - – 50g H_2 Subsystem Evaluations
  - – 1 kg H_2 System Design/Evaluation
  - – 5 kg H_2 System Design/Evaluation
  - – System Modeling

Safety Analysis



TRANSPORT
OF
DANGEROUS GOODS
Manual
of
Tests and Criteria

DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed. (1999).

- Flammability
  - *Flammability Test*
  - *Spontaneous Ignition*
  - *Burn Rate*
- Water Contact
  - *Immersion*
  - *Surface Exposure*
  - *Water Drop*
  - *Water Injection*
- Dust Explosion
  - *P_{max} & $(dP/Dt)_{max}$ (ASTME1226)*
  - *Min. Exp. Conc.(ASTM 1515)*
  - *Min. Ignition Energy (ASTM 2019)*
  - *Min. Ignition Temp.(ASTM 1491)*

CCH#0: 2m%$TiCl_3$
1. Fully Charged, CCH#0-100: *($NaAlH_4$)*
2. Partially Discharged, CCH#0-33: *(Na_3AlH_6+2Al)*
3. Fully Discharged, CCH#0-0: *(NaH+Al)*

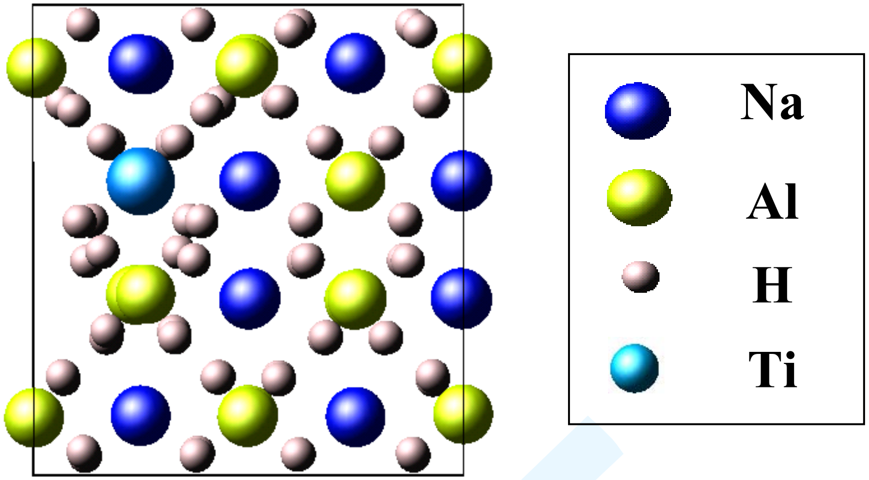
- ***Class 4.3, Packing Group II: No change from uncatalysed material. Spontaneous combustion with water, pyrophoric in air***
- ***Class St-3, Highly Explosive***

Dust Explosion Testing

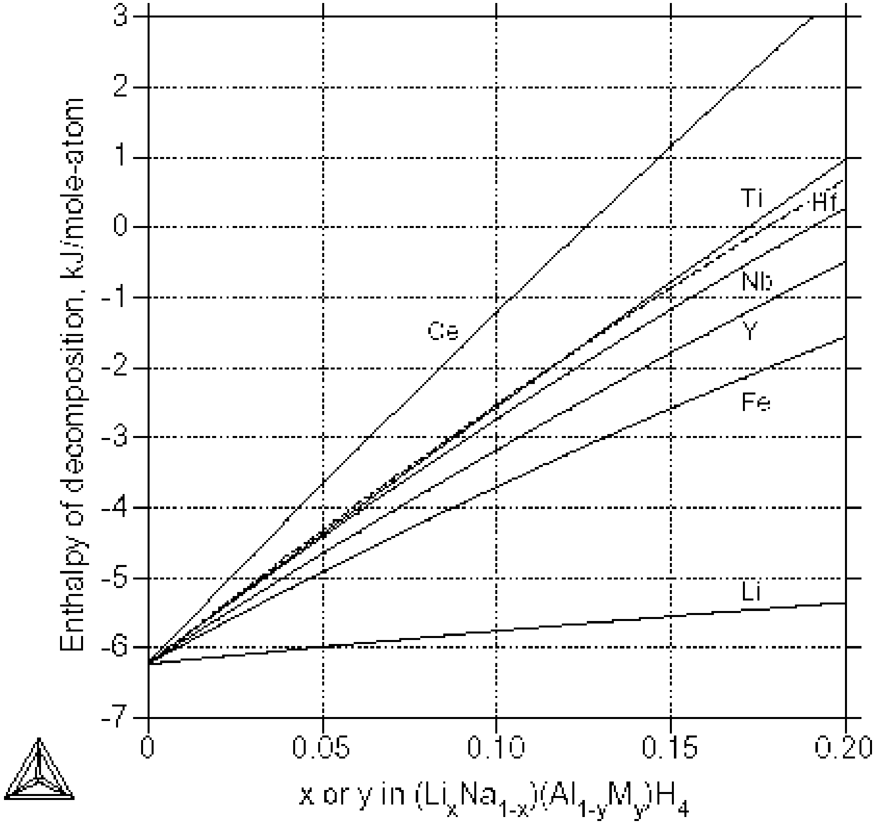
	Test Materials		Reference Materials	
	$NaAlH_4$+ 2% $TiCl_3$	NaH+Al + 2% $TiCl_3$	Pitt. Seam Coal Dust	Lycopodium Spores
P_{max} *bar-g*	11.9	8.9	7.3	7.4
R_{max} *bar/s*	3202	1200	426	511
K_{st} *bar-m/s*	869	326	124	139
Dust Class	St-3	St-3	St-1	St-1
MEC *g/m³*	140	90	65	30
MIE *mJ*	<7	<7	110	17
T_c *°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

Calculated Dissociation Pressures



$Na_{16}TiAl_{15}H_{64}$ Supercell



- Combined Atomistic and Thermodynamic modeling predicts relative activity of catalysts and site substitution as:

$$(Na_{1-y}Am_y)(Tm_xAl_{x-1})H_4$$

or $$(Na_{1-y}Am_y)_3(Tm_xAl_{x-1})H_6$$

QuesTek INNOVATIONS LLC

Kinetics

Materials

Starting Materials

- Commercial purity $NaAlH_4$
- High purity H_2 (99.995 pure)

Primary impurities **N_2**, O_2, CH_4, CO_2, CO, **H_2O**

Compositions

- 6% $TiCl_3$
- 4% $TiCl_3$
- New catalyst/method method
- 4% $CeCl_3$
- 6% TiF_3

Testing

Isobaric Absorption

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

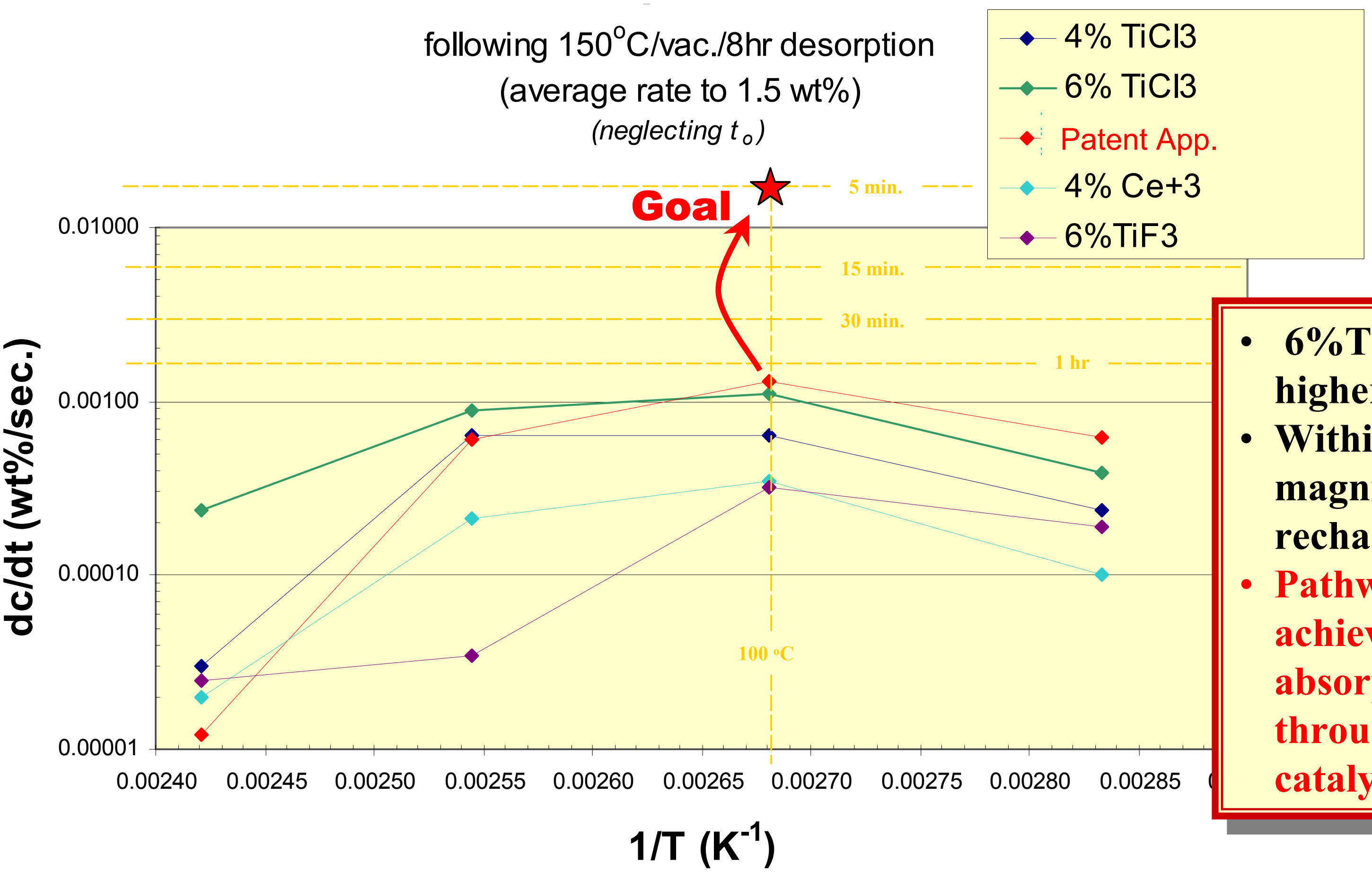
Isobaric Desorption

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

Isothermal Absorption

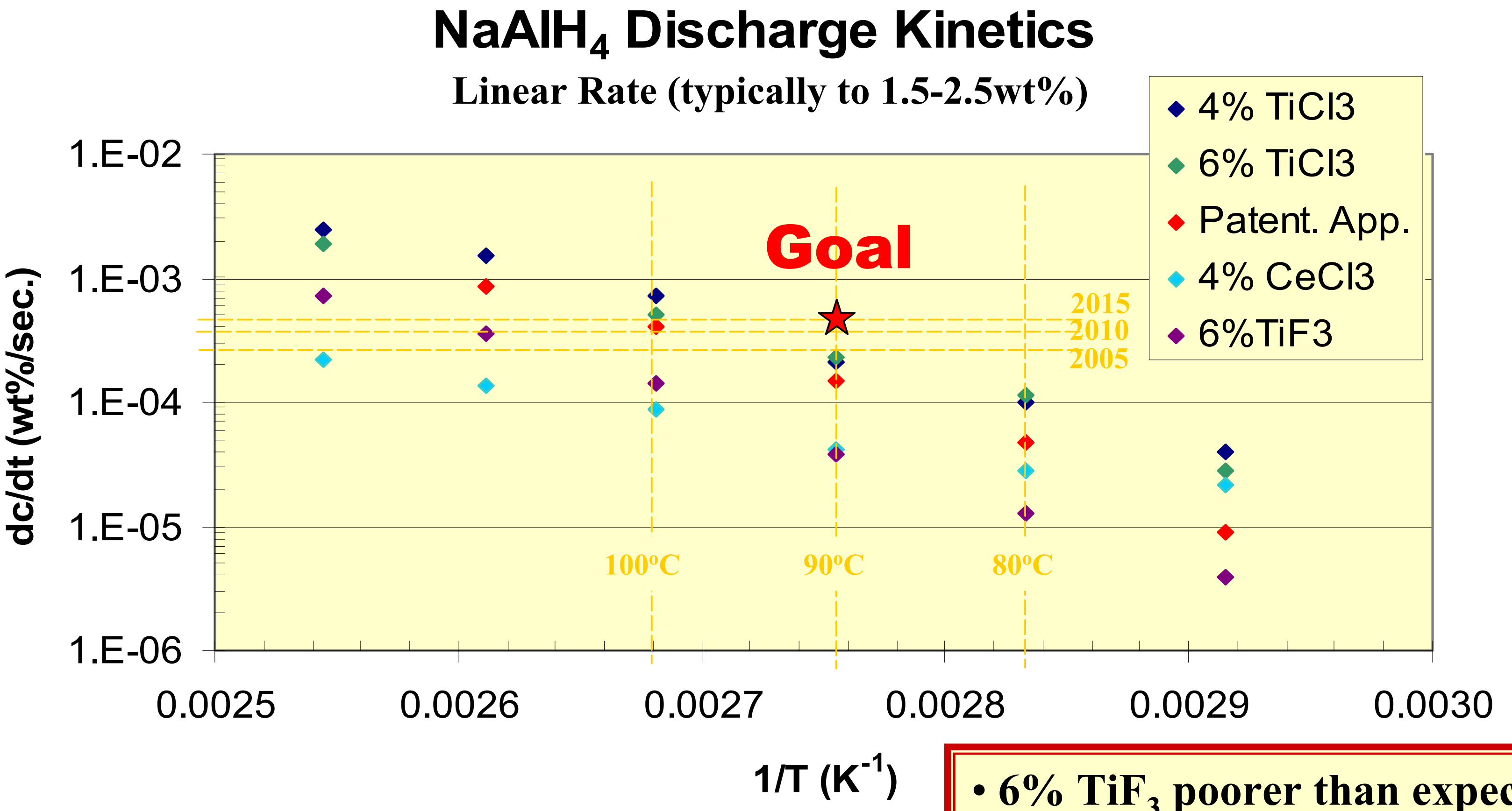
- **150°C/vac/24hrs**
- T = 120°C
- P = 50, 68, 90, 110 bar

Charging Kinetics



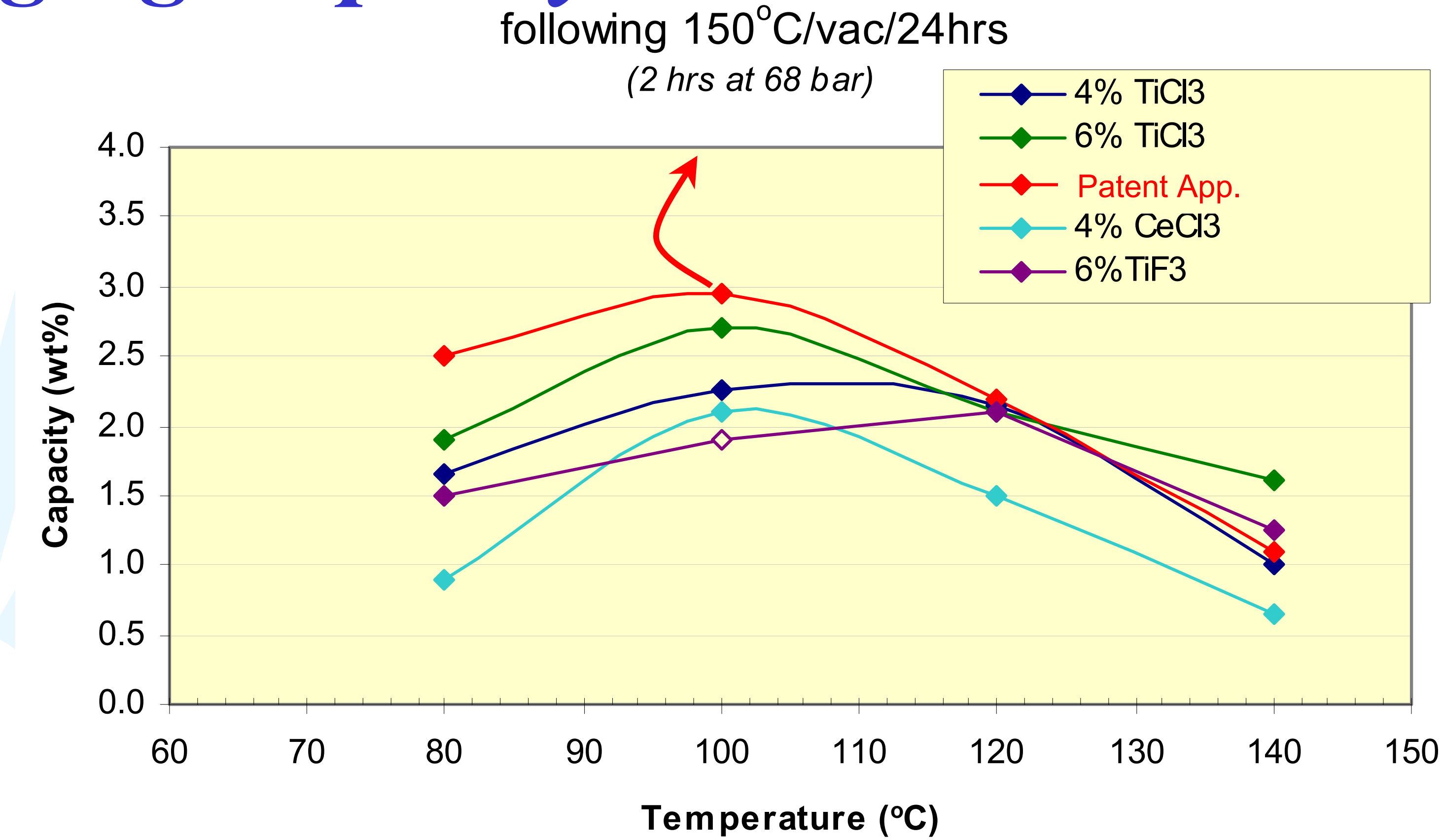
- **6%$TiCl_3$ highest rate at higher temperatures**
- **Within one order of magnitude of 5 min. recharge rate.**
- **Pathway identified to achieve increase absorption kinetics through utilization of new catalyzation technique.**

Discharge Kinetics



- 6% TiF_3 poorer than expected
- 4% $CeCl_3$ poorer than expected
- 4 & 6%$TiCl_3$ comparable at all T's

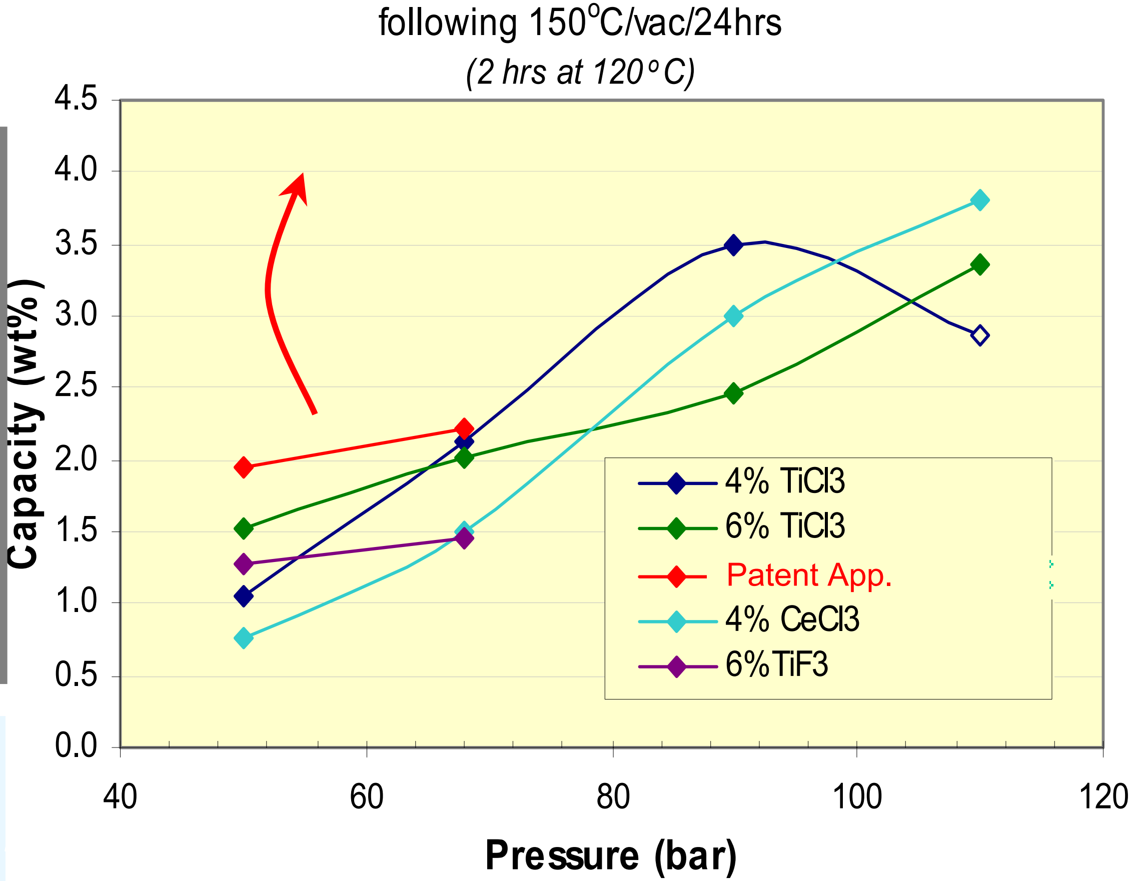
Charging Capacity



- 6% TiF_3 and $TiCl_3$ comparable
- Pathway identified to increase $NaAlH_4$ capacity to ~3.7% or greater if it can be made effective in Na_3AlH_6 desorption.

Pressure Dependence

- **Isochronal evaluations of capacity used as quantification measure**
- **4% MCl_3 have highest pressure dependence *(lower P to max capacity).***
- **New Pathway identified to increase low pressure $NaAlH_4$ capacity**



Cyclic Stability

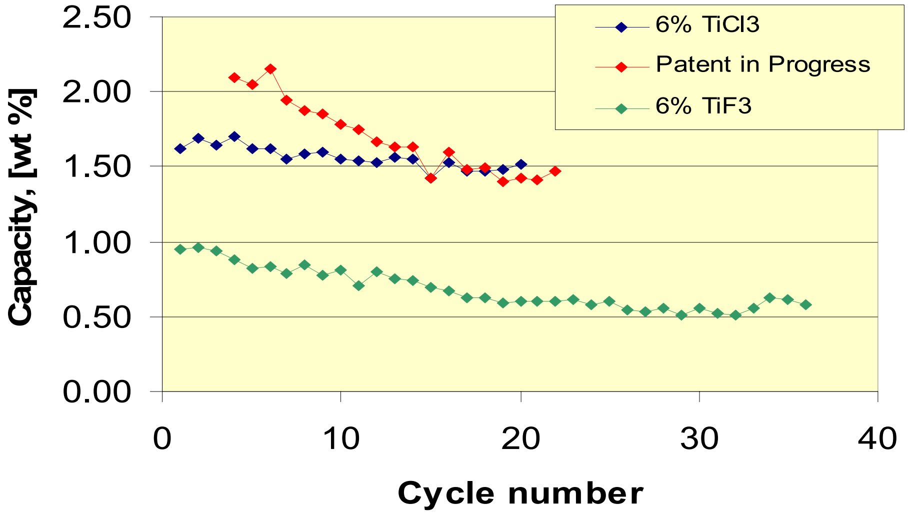
Hydrogen gas impurity effects

Commercial Purity $NaAlH_4$
50g $NaAlH_4$ + 6m%$TiCl_3$
Com. Purity Gas: 99.95% H_2
(typical contaminants: <20ppm N_2, O_2, H_2O, CO, CO_2 & CH_4)

Automated Equipment Limitation

	Pressure *(bar)*	**Temperature *(°C)***	**Time *(hrs)***
Charge Cycle	100	100	4
Discharge Cycle	2	100	8

- Relatively low capacities are artifacts of isothermal testing constraints.
- 10-50% decrease in capacity attributed to H_2 gas impurities.
- <u>No oxides/hydroxides identified by XRD after cycling.</u>



System Overview

Conventional Metal Hydride ($LaNi_5$) vs $NaAlH_4$

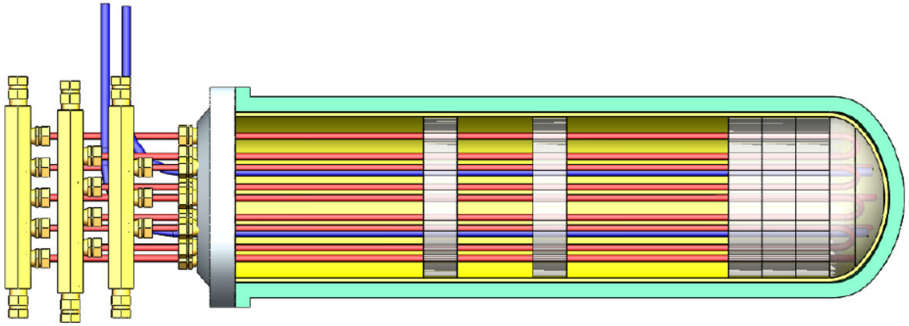
	$LaNi_5$	$NaAlH_4$
Charging pressure	10 atm	50 to 100 atm
Media volumetrics	50 kg H_2 / m^3	25 kg H_2 / m^3 **
Gravimetric goal	(~1%)	6%
Expansion forces	High	Low
Fabrication environment	Air ⇒ activation	Glove box
Powder loading	Controllable	Challenge
Water reactivity	Low	High

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

Composite vessel

Fully open end

Oil HT fluid



1st prototype design - can be disassembled

Heat Transfer Optimization

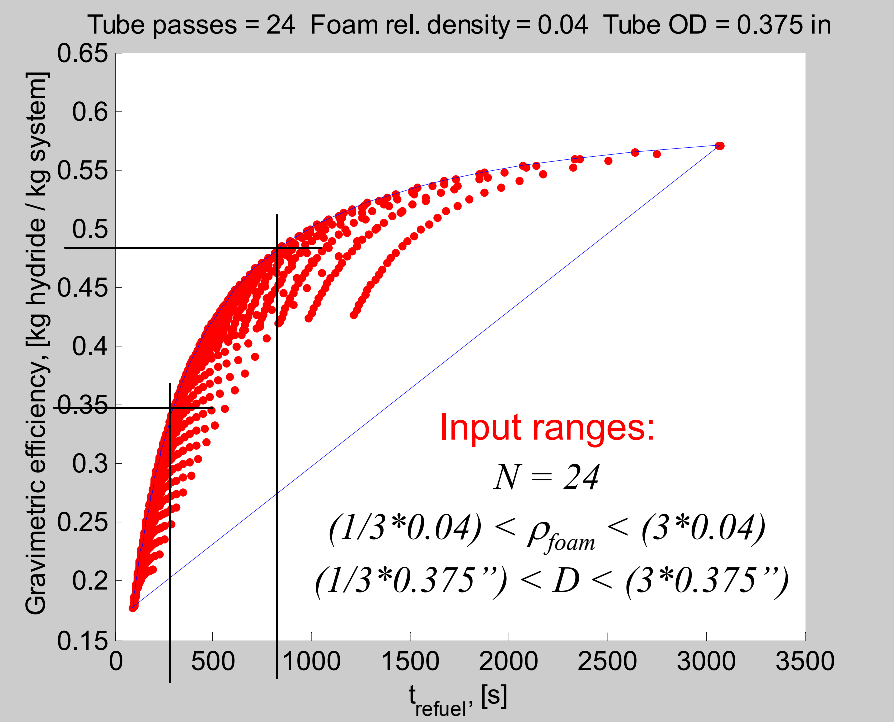
Design inputs

- N: number of tubes
- D: tube diameter
- ρ_{foam}: aluminum foam relative density

Performance outputs:

- ρ_{grav} : gravimetric efficiency
- t_{refuel}: refueling time

Optimal points - convex hull



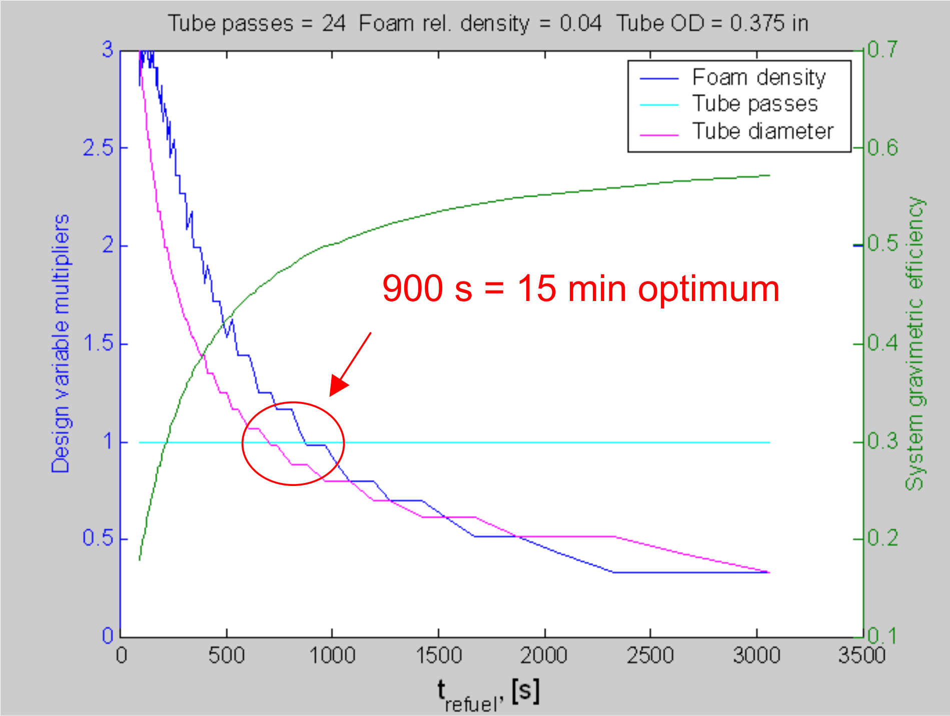
Input ranges:

$N = 24$

$(1/3*0.04) < \rho_{foam} < (3*0.04)$

$(1/3*0.375") < D < (3*0.375")$

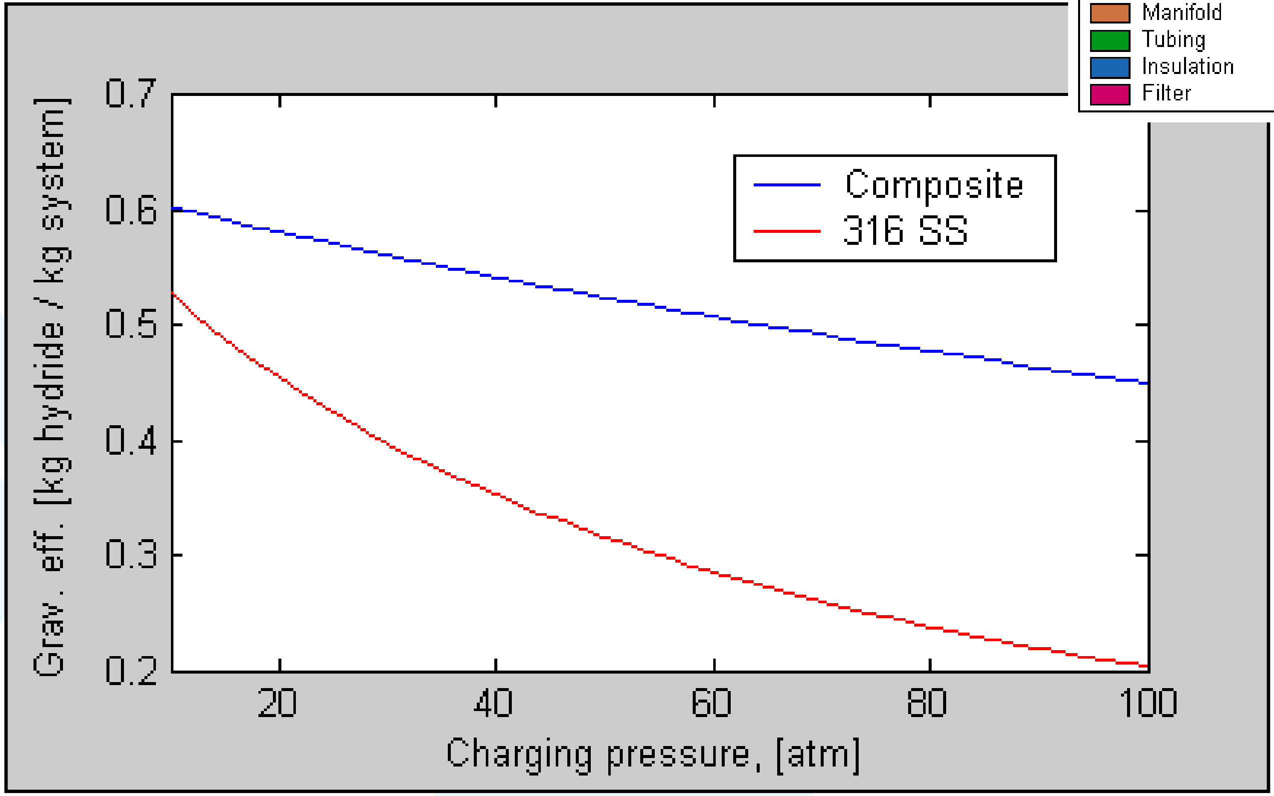
Design variables along convex hull



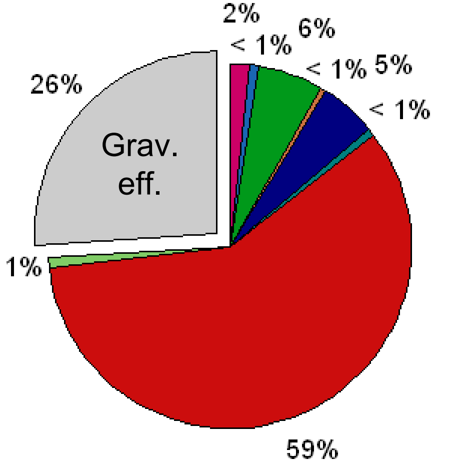
900 s = 15 min optimum

Optimal design: 24 tubes of 3/8" diameter with 4% dense aluminum foam

Gravimetric Efficiency



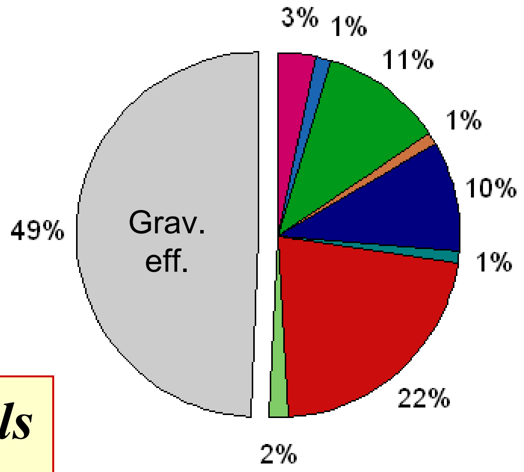
316 Stainless steel



- ⬜ Hydride
- 🟩 Oil
- 🟥 Pressure Vessel
- 🟦 Supports
- 🟦 Conduction Enh.
- 🟧 Manifold
- 🟩 Tubing
- 🟦 Insulation
- 🟪 Filter

350 Wh / kg 500 Wh / L

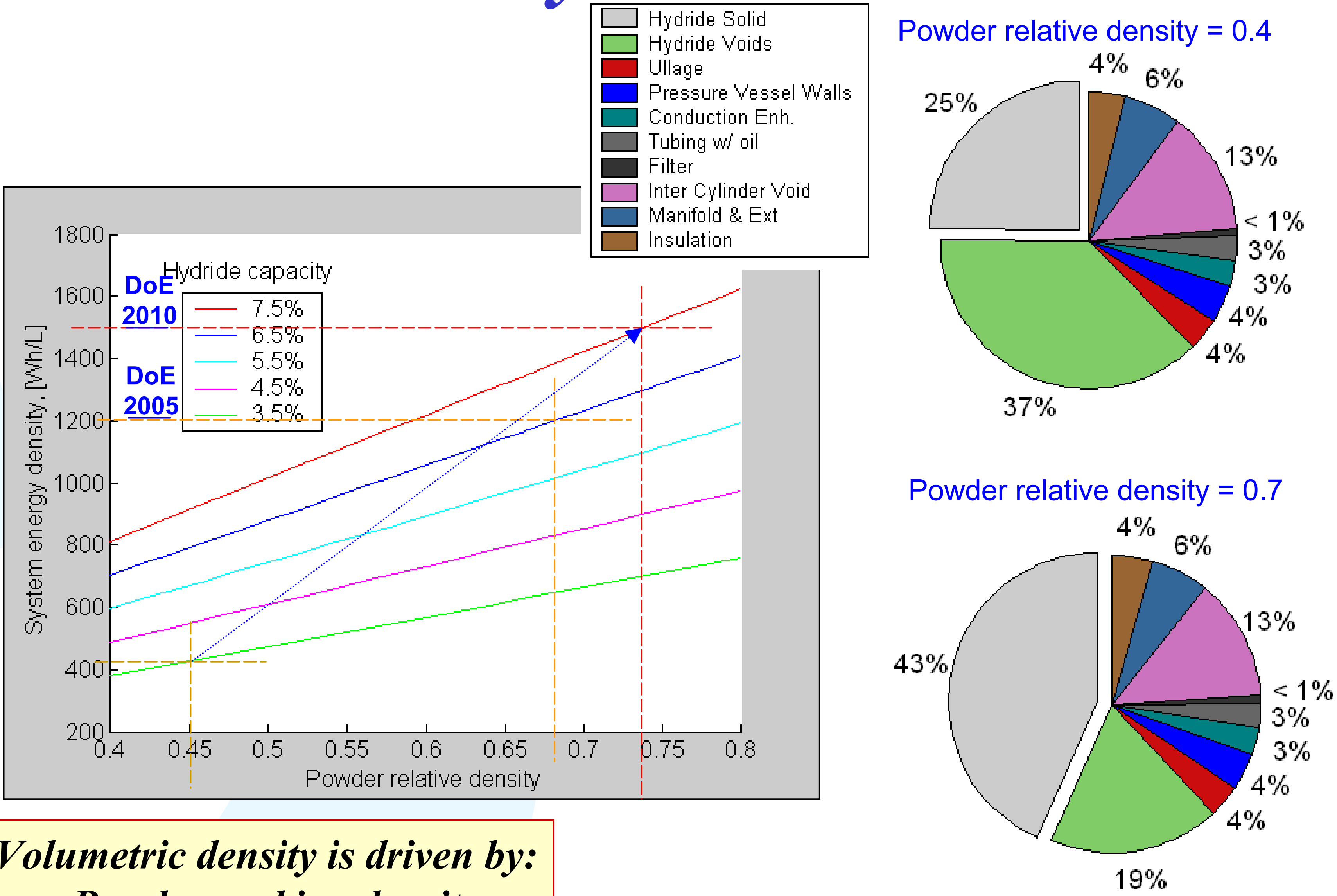
Carbon fiber composite



60 Wh / kg 530 Wh / L

- ***Composite vessel necessary to approach gravimetric goals***
- ***Mass of heat transfer structures motivates optimization***

Volumetric Density

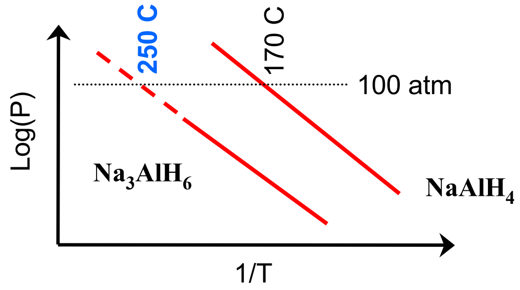


- *Volumetric density is driven by:*
  - *Powder packing density*
  - *Gravimetric density*

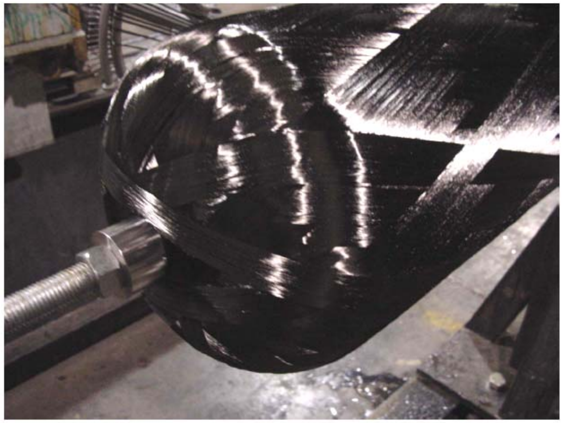
Composite Vessel

Specifications:

- **250°C:** high temperature resin
- **100 atm** working pressure
- **40”** length, **9.5”** inner diameter
- **Stainless steel** liner
- Parr Instruments **stainless steel lid** for easy removal and inspection after evaluation.
- Designed to meet **ASME section 10** pressure vessel code
- **FEM analysis** performed to insure safety factor at design pressure.



filament winding

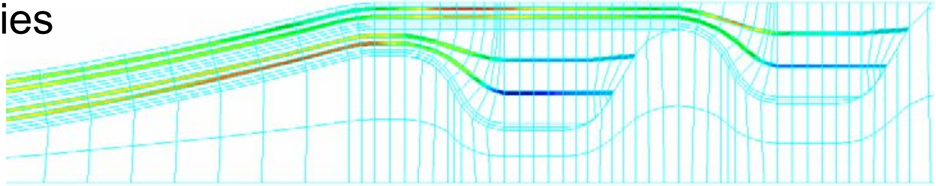


SCC Spencer Composites Corporation

Vendor:

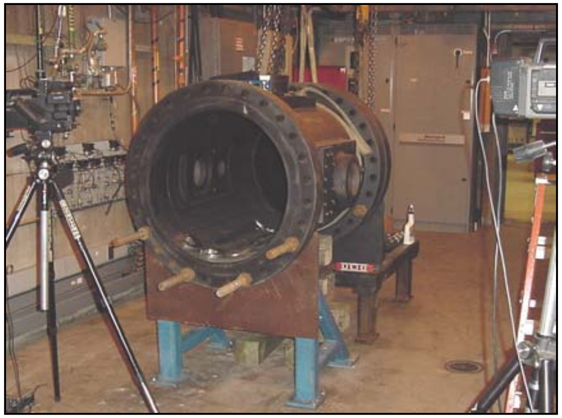
- Custom design & fabrication
- Specialty production
- Full open, closed one end & high temperature design and fabrication experience
- Supplier to aerospace and petroleum industries

Flange - composite interface



Safety is top concern in all designs and evaluations

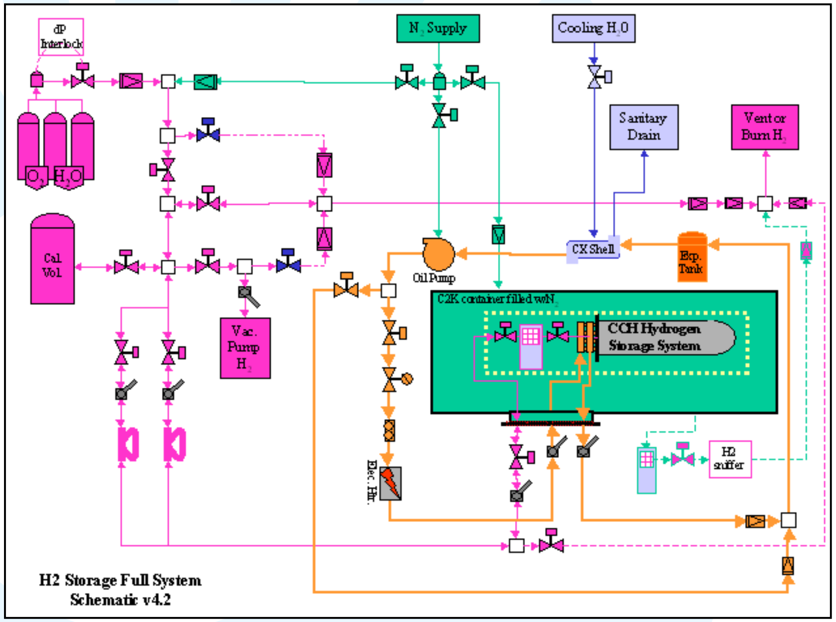
1 kg System Testing



Testing will utilize UTRC’s Combustion research facility

- 18” thick reinforced concrete walls and ceiling
- Sheet metal directed blow-out back wall
- Secondary pressure vessel within test cell
- External control & monitor station

Test apparatus design complete



Hosted DoE Hydrogen Safety Review Committee on May 5, 2004.

Safety is top priority in testing of first prototype.

System Level Modeling

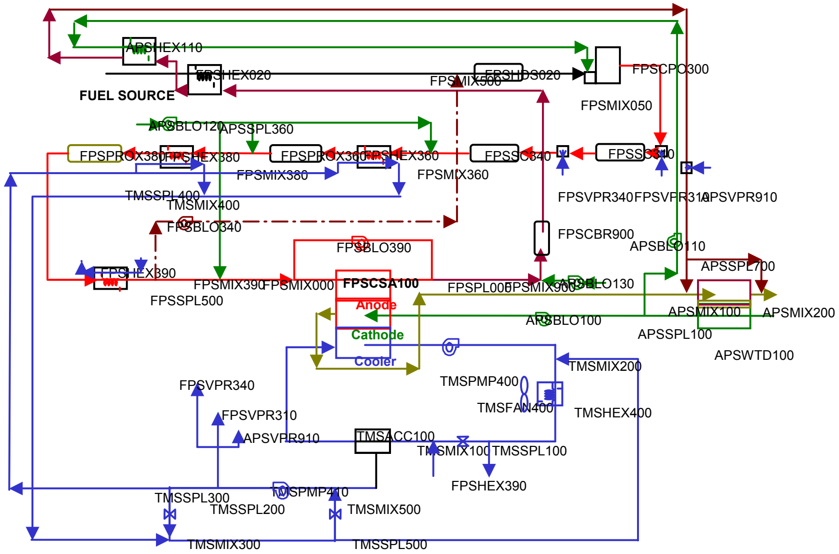
gPROMS

- Steady state modeling
- Detailed reactor simulation

DYMOLA

- Dynamic system modeling
- Control logic implementation

FPS/Cell Stack Integration



Status

–System models constructed and base line performance quantified.

–System integration concepts and preliminary models have been generated.

– Results are considered sensitive IP.

System Projections

optimized $NaAlH_4$ *(0.5wt% improvement)*

New material discovery *or full NaAlH4 (1wt% improvement)*

Hydrogen Storage System
Predicted Performance Metrics

	Symbol	units	CCHSS#1	CCHSS#1.1	CCHSS#2	DoE	DoE	UTRC
	Media		4m%TiF_3	improved $NaAlH_4$	5.5% media - '05	2005 Goal	2010 Goal	2004 Goal
Media Density	ρ^m	*g/cm^3*	1.28	1.28	1.28			
Media Gravimetric Density	ρ^m_g	*wt%*	4.0%	**4.5%**	**5.5%**			
Media Volumetric Density	ρ^m_v	*kgH_2/m^3*	51.2	57.6	70.4			
System Gravimetric Density	ρ^s_g	*wt%*	**2.4%**	**2.9%**	**4.4%**	**4.5%**	**6.0%**	**3.0%**
"	ρ^s_g	*kWh/kg*	*0.8*	*1.0*	*1.5*	***1.50***	***2.00***	***1.00***
System Volumetric Density	ρ^s_v	*kgH_2/m^3*	**15.4**	**20.6**	**35.9**	**36.0**	**45.0**	**16.5**
"	ρ^s_v	*kWh/l*	*0.51*	*0.69*	*1.20*	***1.20***	***1.50***	***0.55***
Media Charging Rate	r^m_C	*wt%/hr*	14.3	16.2	33.0			
Media Discharging Rate	r^m_D	*wt%/hr*	0.9	1.1	12.0			
System Charging Rate	r^s_C	*wt%/hr*	14.3	16.2	33.0			
System Discharging Rate	r^s_D	*wt%/hr*	0.9	1.1	12.0			
Gravimetric Engineering Efficeincy	E^g		**0.6**	**0.65**	**0.8**			
Volumetric Engineering Efficiency	E^v		0.5	**0.55**	**0.68**			
Powder Packing density	ρ^m_p		0.6	**0.65**	**0.75**			
Heat Transfer Coefficient	κ^s_f		1.0	1.0	1.0			
System Capacity	C^s	*kgH_2*	5.0	5.0	5.0	**5**	**5**	**5**
System Charging Rate	R^s_C	*kgH_2/hr*	**17.9**	18.0	30.0	**30**	**90**	**18**
System Discharging Rate	R^s_D	*kgH_2/hr*	**1.18**	1.22	10.91	**10.8**	**14.4**	**1.2**
Media Mass	m^m	*kg media*	125.0	111.1	90.9			
System Mass	m^s	*kg sys.*	208.3	170.9	113.6			
Media Volume	v^m	*m^3*	0.10	0.09	0.07			
System Volume	v^s	*m^3*	*0.195*	*0.158*	*0.104*			
System Volume	v^s	*gal.*	51.6	41.7	27.6			

media
system

new design *(5 pt savings)*
system approach *(10 pt. savings)*

new fill method *(10 pt savings)*

improved HX design *(5 pt savings)*

improved fill method *(5 pt savings)*

Going Forward Plan

- Safety Analysis
- Atomistic/Thermodynamic Modeling
- 50g H_2 Prototype System
- Media Kinetic Characterization
- Media Kinetic Modeling
- Heat/Mass Transfer Analysis
- High Temp. Composite Tank Development
- 1kg H_2 Prototype/Evaluation
- ~~5kg H_2 Prototype/Evaluation~~
- ~~5kg Prototype Delivery~~

1kgH_2 CCHSS#1.1

System Design
  New filling & HX method
New $NaAlH_4$ catalyst method
  Higher capacity within P & T

1kgH_2 CCHSS#2

System Design
  2-end semi-closed composite tank
  New mfg. method
  New filling method
  Metalized polymer liner
System Modeling
Improved $NaAlH_4$ catalysts
  Lower charging pressure

Partners

- **UTPower: Automotive PEMFC requirements & system models.**
- **Hydrogen Components Inc.: F.L. Lynch – safety testing, system design and fabrication.**
- **QuesTek: Prof. G. Olsen & Dr. C. Qiu – thermodynamic modeling.**
- **Albemarle: Dr. J. Powers – $NaAlH_4$ properties, handling, and impurity content effects.**
- **U. Hawaii: Prof. C. Jensen – Consultation on $NaAlH_4$ properties and capabilities.**
- **IFE: Dr. O.M. Lovvik – Atomistic simulations.**
- **Spencer Composites, LLC: B. Spencer – High temperature & pressure graphite reinforced composite tank design and fabrication.**

Previous Year's Comments

- **Comment**

  "Weakness is that this will not meet low goals."

We are designing and building the best possible hydrogen storage system possible with existing materials to learn fundamental concepts in utilizing alanate materials and in anticipation of future materials invention.

- **Comment**

  "Maintain sufficient latitude in the design to accommodate other reversible H_2 sorbents …"

This is the stated strategy.

Future Work

- Complete fabrication of 1 kg H_2 system, CCHSS#1.
- Complete evaluation of CCHSS#1 under charging, discharging and conditions.
- Tear down CCHSS#1 to evaluate system deterioration.
- Design/evaluate advanced HX concepts for integration into CCHSS#1.1
- Design/evaluate new composite fabrication technologies into CCHSS#2

Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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Merit Review
Philadelphia, PA
May 24-27, 2004

Rev. A

Objective

To assist DoE in the development of **new complex hydride compounds capable of reversibly storing hydrogen to a capacity of $\geq$7.5 wt %** and regeneration for 500 cycles with 100 % recovery.

Approach

Discover new reversible high hydrogen content complex hydride compounds, $Na_yM^{+i}_x(AlH_4)_{y+ix,}$ in the quaternary phase space between sodium hydride (NaH), alane (AlH_3), transition metal or rare earth (M) hydrides (MH_z, where z= 1-3) and molecular hydrogen (H_2) utilizing Solid State Processing (SSP), Molten State Processing (MSP) and Solution Based Processing (SBP).

$$Na_yM^{+i}_x(AlH_4)_{y+ix,}$$

Budget

Total Funding: $2.9M *(27% cost share)*

FY '04: *$569,000*

SRTC CRADA: *$150,000*

Duration: 3 years

Start:

Signed: March 17, 2004
UTRC anticipatory: December 1, 2003

Technical Barrier & Targets

	Metric	*Units*	2005 DoE Goal	2010 DoE Goal	UTRC GO/NoGo
	Capacity	*kg*		5	
H_2 Storage Density	Gravimetric	*kWh/kg*	1.5	2	2.00
	Volumetric	*kWh/l*	1.2	1.5	
Cost	Total life cycle (15 yr/150k miles)	*\$(03)/kWh*	6.00	4.00	
	Fuel (gasoline equivilent)	*\$(01)*	3.0	1.3	
	Marginal Fuel Cost (Ref. \$1/kWh for H_2)	*\$(03)/kg*H_2	NA	1.5	
Operating Temperature	Min.	*°C*	0	-30	
	Max.	*°C*	50	50	
Cycle Life	Cycle Life (0.25-100%)	*N*	500	1000	
	Mean	%	N/A	90	
	Confidence	%	N/A	90	

	Metric	*Units*	2005 DoE Goal	2010 DoE Goal	UTRC GO/NoGo
Hydrogen Delivery	Max. H_2 Delivery Temp.	*°C*	100		
	Min. H_2 Delivery Temp.	*°C*	-20	-30	
	Min. Full Flow	*g* H_2*/sec.*	3.0	4.0	
	FC Min. Pressure	*kPa/bar*	250/2.5	250/2.5	
	ICE Min. Pressure	*kPa/bar*	1000/10	3500/35	
	Purity	*% (dry)*	99.9	99.9	
Transient Response	0-90% 90-0%	*sec.*	0.5	0.5	
	start to full flow @20°C	*sec.*	4.0	0.5	
	start to full flow @-20°C	*sec.*	8.0	4.0	
	Refueling Rate	*kg* H_2*/min.*	0.5	1.5	
	Loss of Useable H_2	*g/hr kg* H_2	1.0	0.1	
	Permeation & Leakage	*scc/hr*	*Federal enclosed-area safety standard*		
	Toxicity		*Meets or exceeds applicable standards*		
	Safety		*Meets or exceeds applicable standards*		

7.5 wt% media is required for a 2kWh/ℓ system!

Mixed Complex Hydride Candidates

$NaAlH_4 \cdot M^{+x}(AlH_4)_x$

Table I

Known Alanate Compounds

CAS No.	Composition	Mol. Wt.	wt.%H2	x *
123951-44-(	$Be(AlH_4)_2$	71.04	**8.45**	2
17300-62-8	$Mg(AlH_4)_2$	86.33	**6.95**	2
16941-10-9	$Ca(AlH_4)_2$	102.11	**5.88**	2
43736-89-6	$Sr(AlH_4)_2$	149.65	**4.01**	2
16853-85-3	$LiAlH_4$	37.95	**7.91**	1
13770-96-2	$NaAlH_4$	54.00	**5.56**	1
16903-34-7	$KAlH_4$	70.10	**4.28**	1
19414-22-3	$RbAlH_4$	116.68	**2.57**	1
16961-92-5	$CsAlH_4$	171.13	**1.75**	1
56508-67-9	$Ti(AlH_4)_4$	171.95	**8.14**	2
62866-04-0	$Y(AlH_4)_3$	181.95	**5.50**	2
26042-21-7	$Nb(AlH_4)_3$	185.95	**5.92**	

Table II

Proposed Alanate Compounds

Composition	Mol. Wt.	wt.%H2	x *
$V(AlH_4)_4$	175.00	**8.57**	1
$Cr(AlH_4)_6$	238.08	**9.66**	1
$Mn(AlH_4)_6$	241.02	**9.13**	2
$Fe(AlH_4)_3$	148.89	**8.06**	0
$Co(AlH_4)_3$	151.97	**7.90**	0
$Nb(AlH_4)_5$	247.98	**7.66**	1
$Mo(AlH_4)_6$	282.02	**7.80**	2

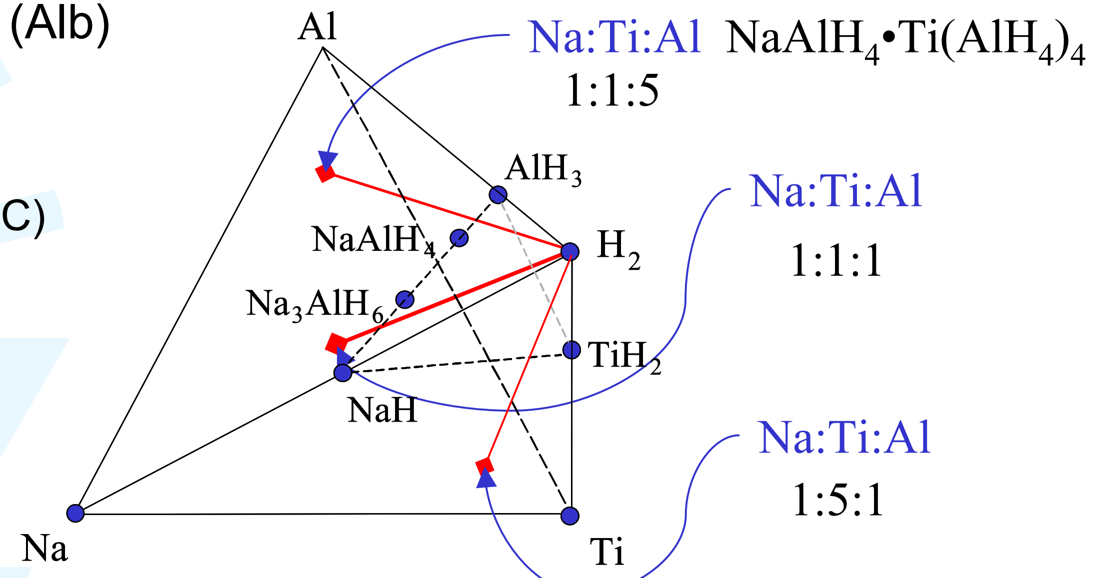
Start Here!
Year #1

If Unsuccessful
Move on!
Year #2

Program Outline

- First Principals Modeling (UTRC)
  - Known Alanate Structures
  - Known $NaAlH_4$ Catalysts
  - Compound Prediction
- Synthesis
  - Solid State Proc.(UTRC)
  - Molten State Proc. (SRTC)
  - Solute Based Processing (Alb)
- Analysis
  - Structure
    - XRD (all), TRXRD (UTRC)
    - ND (IFE)
  - Calorimetry (Alb)
- Performance
  - Van’t Hoff (UTRC)
  - Kinetics (UTRC)
- Cyclic Stability (UTRC)
- Scale-Up (Alb)
- Business Analysis (UTRC, Alb)

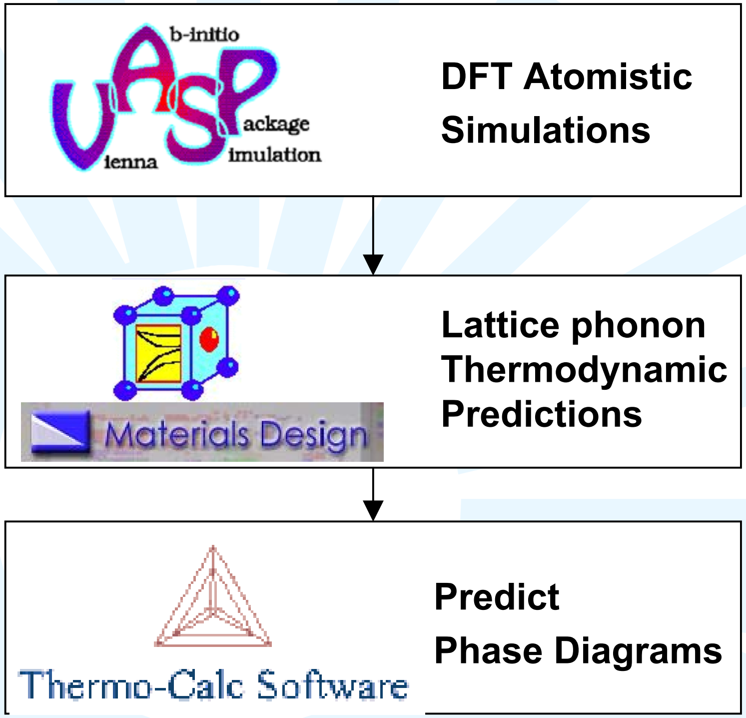
Initial Composition Approach



First Principals Modeling

OBJECTIVE:

Understand the atomistic and thermodynamic principals of complex hydride materials. Use this understanding to predict new high hydrogen capacity complex hydride phases.



DFT Atomistic Simulations

Conduct atomistic simulations to screen and identify high hydrogen capacity quaternary complex hydride phases at 0K.

Lattice phonon Thermodynamic Predictions

Predict temperature dependant thermodynamic properties.

Predict Phase Diagrams

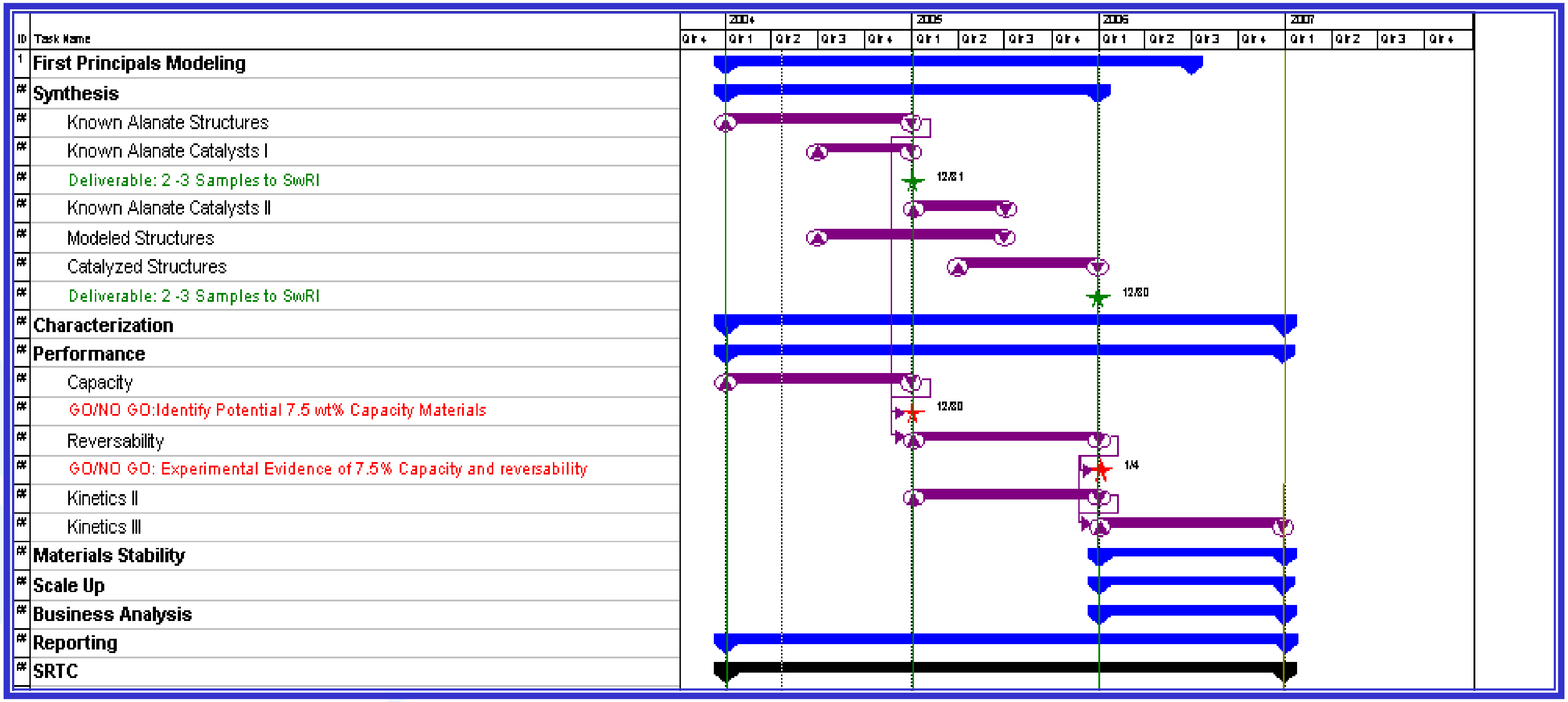
Conduct thermodynamic calculations to predict phase relationships in selected phase fields and pressure-composition isotherm relationships.

Safety

- Quantification of the safety risks associated with synthesis, storage and testing of high hydrogen containing compounds and their associated powders and solvents.

- Identification of safety vulnerabilities and risk mitigation strategies in:
  - Synthesis, characterization and testing of laboratory quantities of AlH_3, $Mg(AlH_4)_2$ and similar compounds
  - Scaled up to 1 kg quantities of promising compounds via most cost effective processing route.

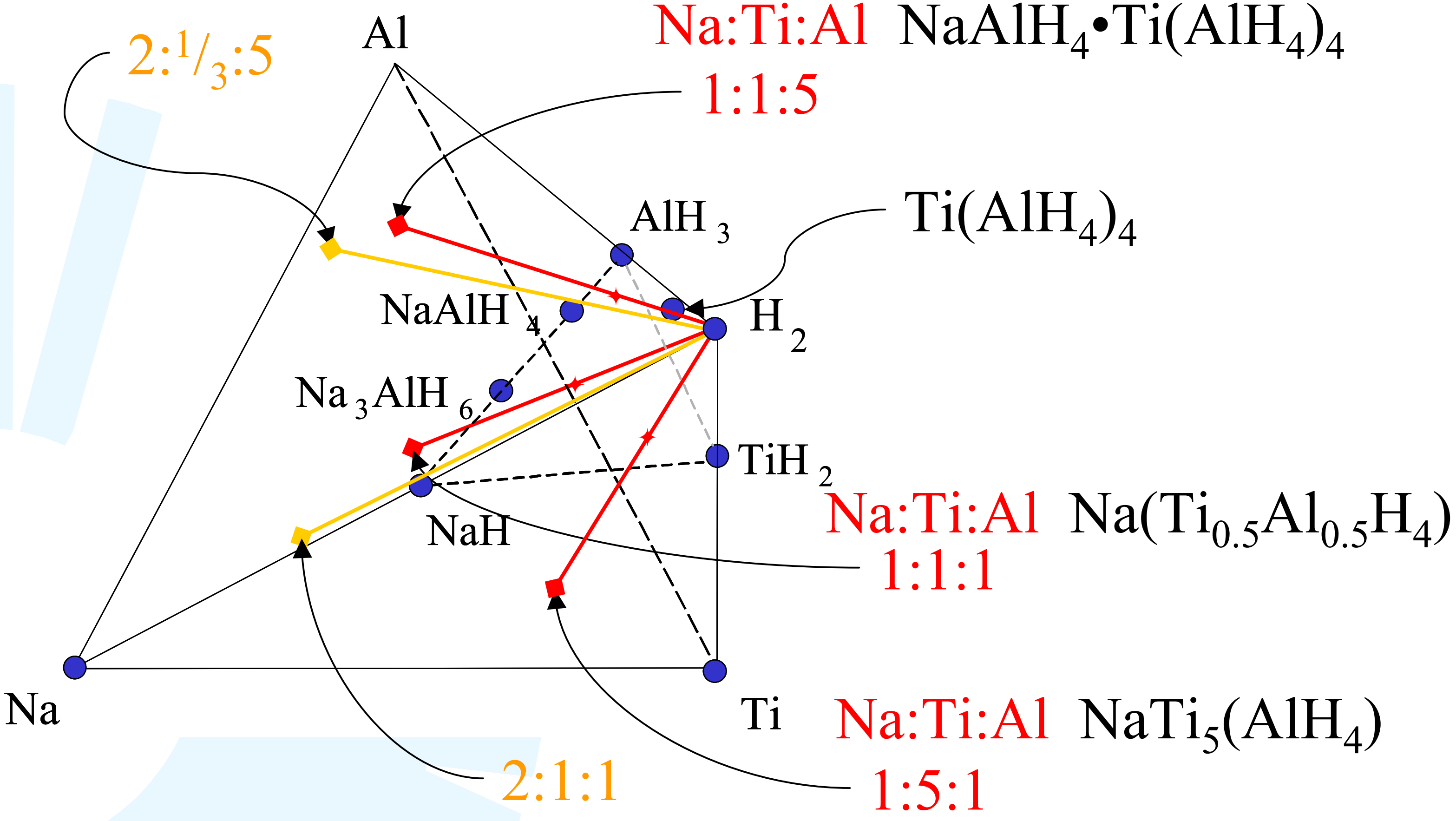
Timeline



ID	Task Name
1	**First Principals Modeling**
#	**Synthesis**
#	Known Alanate Structures
#	Known Alanate Catalysts I
#	Deliverable: 2 -3 Samples to SwRI
#	Known Alanate Catalysts II
#	Modeled Structures
#	Catalyzed Structures
#	Deliverable: 2 -3 Samples to SwRI
#	**Characterization**
#	**Performance**
#	Capacity
#	GO/NO GO:Identify Potential 7.5 wt% Capacity Materials
#	Reversability
#	GO/NO GO: Experimental Evidence of 7.5% Capacity and reversability
#	Kinetics II
#	Kinetics III
#	**Materials Stability**
#	**Scale Up**
#	**Business Analysis**
#	**Reporting**
#	**SRTC**

- Modeling
- Synthesis
- Characterization
- Performance
- Stability
- Scale-Up
- Business Analysis

Composition Ratios



$2:{}^{1}/_{3}:5$

Na:Ti:Al $NaAlH_4 \bullet Ti(AlH_4)_4$
1:1:5

$Ti(AlH_4)_4$

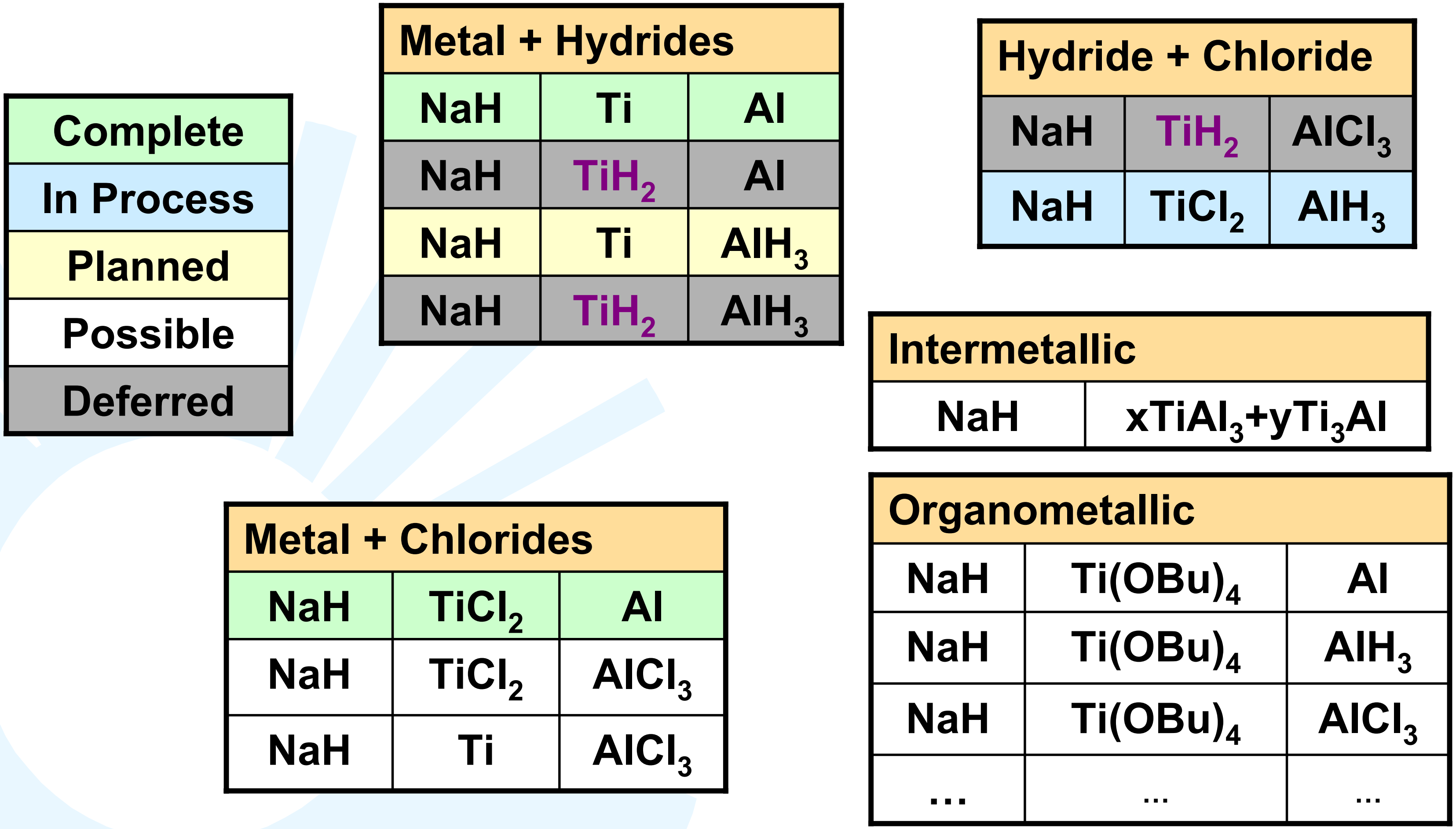
Na:Ti:Al $Na(Ti_{0.5}Al_{0.5}H_4)$
1:1:1

Na:Ti:Al $NaTi_5(AlH_4)$
1:5:1

2:1:1

Possible Sources of Cations

Need to select 2-4 candidates for future experiments.



Complete
In Process
Planned
Possible
Deferred

Metal + Hydrides		
NaH	Ti	Al
NaH	TiH_2	Al
NaH	Ti	AlH_3
NaH	TiH_2	AlH_3

Hydride + Chloride		
NaH	TiH_2	$AlCl_3$
NaH	$TiCl_2$	AlH_3

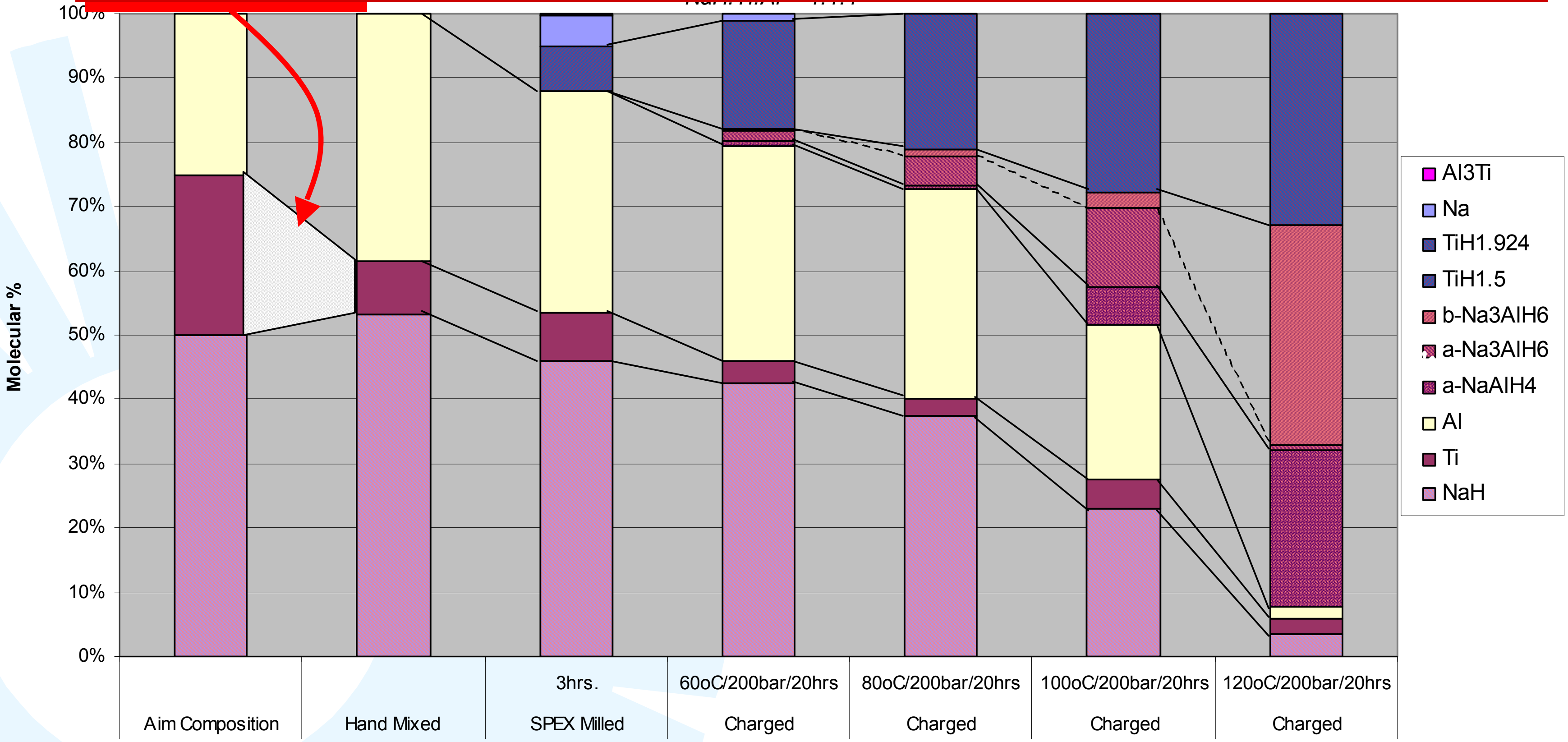
Intermetallic	
NaH	$xTiAl_3+yTi_3Al$

Metal + Chlorides		
NaH	$TiCl_2$	Al
NaH	$TiCl_2$	$AlCl_3$
NaH	Ti	$AlCl_3$

Organometallic		
NaH	$Ti(OBu)_4$	Al
NaH	$Ti(OBu)_4$	AlH_3
NaH	$Ti(OBu)_4$	$AlCl_3$
…	…	…

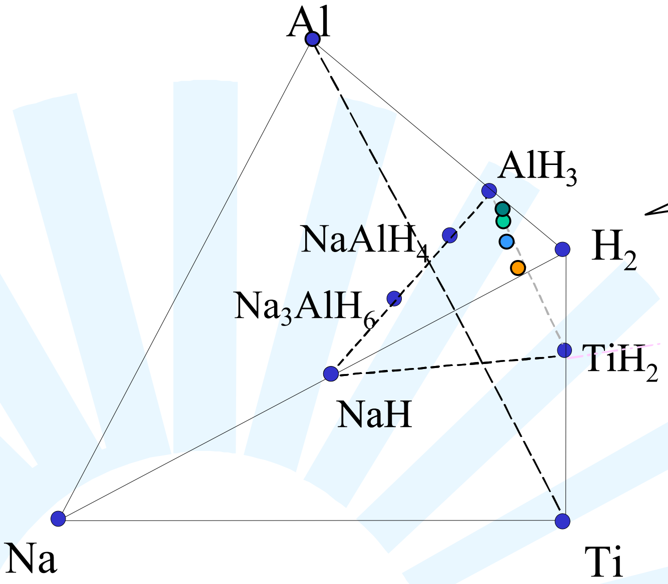
2:1:1 (NaH:Ti:Al) XRD Results

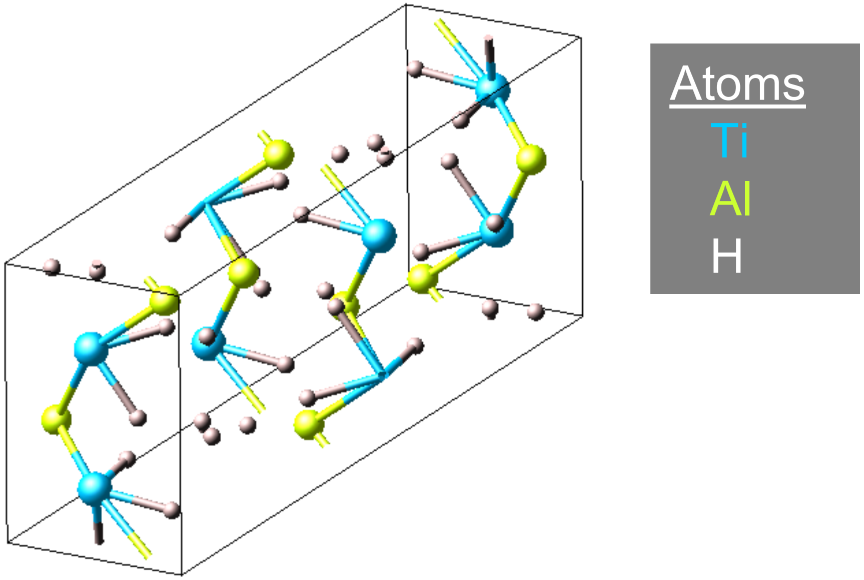
- **Ti concentration is significantly diminished after only hand mixing, due to absorption.** Partial answer as to: *Where is the Ti?*
- **TiH_x strongly bound and not participatory in alanate formation.**



Atomistic Screening of High Capacity Na-Ti-Al-H Analogs

Structural Analogs	Wt.% H_2
$Ti^{+2}(AlH_4)_2^{-2}$	7.2
$Ti^{+3}(AlH_4)_3^{-3}$	8.6
$Ti^{+4}(AlH_4)_4^{-4}$	9.4
$Na^{+1}Ti^{+3}(AlH_4)_4^{-4}$	8.2





Output Structure:$Ti(AlH_4)_2$ C2/c

Thermodynamic Predictions
Screening Criteria
Phase Mapping

Interactions and Collaborations

ALBEMARLE® CORPORATION

ife Institutt for energiteknikk

Savannah River Technology Center
SRTC
We Put Science to Work

- **Albemarle:** Drs. J. Strickler, F.-J. Wu, J.E. Boone, – solute based synthesis, scale-up, safety and business analysis.
- **IFE:** Drs. B. Hauback, H. Brinks &. O.M. Lovvik – Neutron Diffraction, High Resolution XRD & Atomistic simulations.
- **SRTC:** R. Zidan & T. Motyka - high pressure/high temperature synthesis & characterization.

PDC Laboratories

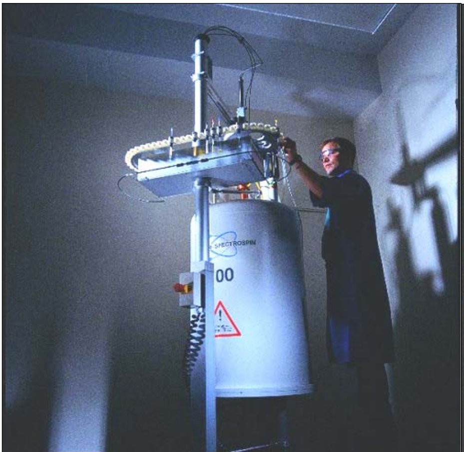
ALBEMARLE®
CORPORATION

Capability

- Bench-scale inert atmosphere process labs
- High-pressure laboratory with 1-10 gal autoclaves
- Reaction calorimeter
- NMR, Mass Spec.
- Pilot plant facilities with 50-300 gal. reactors

Yr 1 Plan

- Literature Review
- Define target compositions
- Develop wet chemical synthesis methods
- Perform preliminary structural characterizations
- Deliver novel ternary alanate samples for evaluation

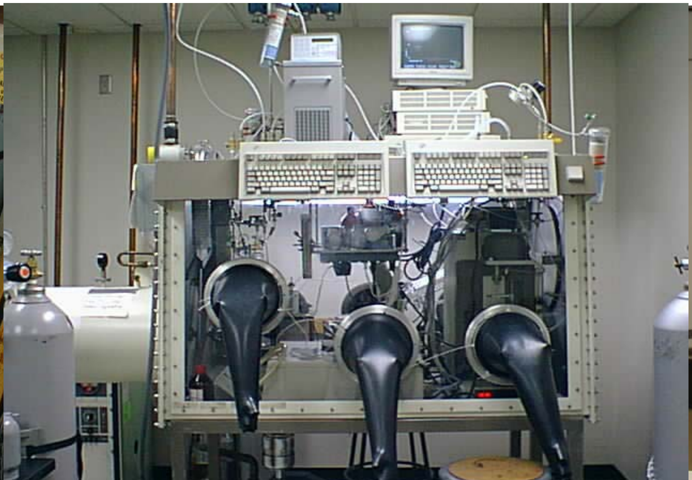


Capability

- High Pressure Synthesis
- Inert Atmosphere TGA, DSC
- Alanate Purification

Yr 1 Plan

- High pressure/temperature synthesis of new complexes
- Enhancement of H_2 sorption kinetics.
- Thermodynamic and energetic calculations and characterization.
- Spectroscopic study of surface and bulk structures.



Future Work

- Complete Na/Ti/Al, Na/Li/Al & Na/Mg/Al and initiate Na/Tm/Al quaternary phase determinations utilizing combined atomistic/thermodynamic modeling approach.
- Complete Na/Ti/Al, Na/Li/Al & Na/Mg/Al and initiate Na/Tm/Al quaternary phase determinations utilizing Solid State Processing (SSP).
- Initiate similar Molten State Processing (MSP) at SRTC.
- Initiate similar Solute Based Processing (SBP) at Albemarle.