Chemical Hydrogen Rate Modeling, Validation, and System Demonstration

Troy A. Semelsberger (P.I.)

Ben L. Davis, Brian D. Rekken, Biswajit Paik, Eric Brosha, and Jose I. Tafoya

DOE Fuel Cell Technologies Program Annual Merit Review,
Washington, DC June 16-20, 2014

Project ID: ST007

Overview

Timeline

- Project Start Date: Feb FY09
- Project End Date: FY14
- Percent Complete: 91%

Budget

- Total Project Funding: $4.1M
  - DOE Share: $4.1M
- Funding:
  - 2013: $880K
  - 2014: $525K

Barriers

A. System Weight and Volume
B. System Cost
C. Efficiency
D. Durability/Operability
E. Charging/Discharging Rates
G. Materials of Construction
H. Balance of Plant Components
J. Thermal Management
K. System Life-Cycle Assessments
R. By-Product/Spent Material Removal

Partners

Overall Objectives/Relevance

DOE COMPASS

1. Develop chemical hydrogen storage system models √⁻
2. Develop chemical hydrogen storage material property guidelines √
3. Develop and demonstrate “advanced” engineering concepts/components √

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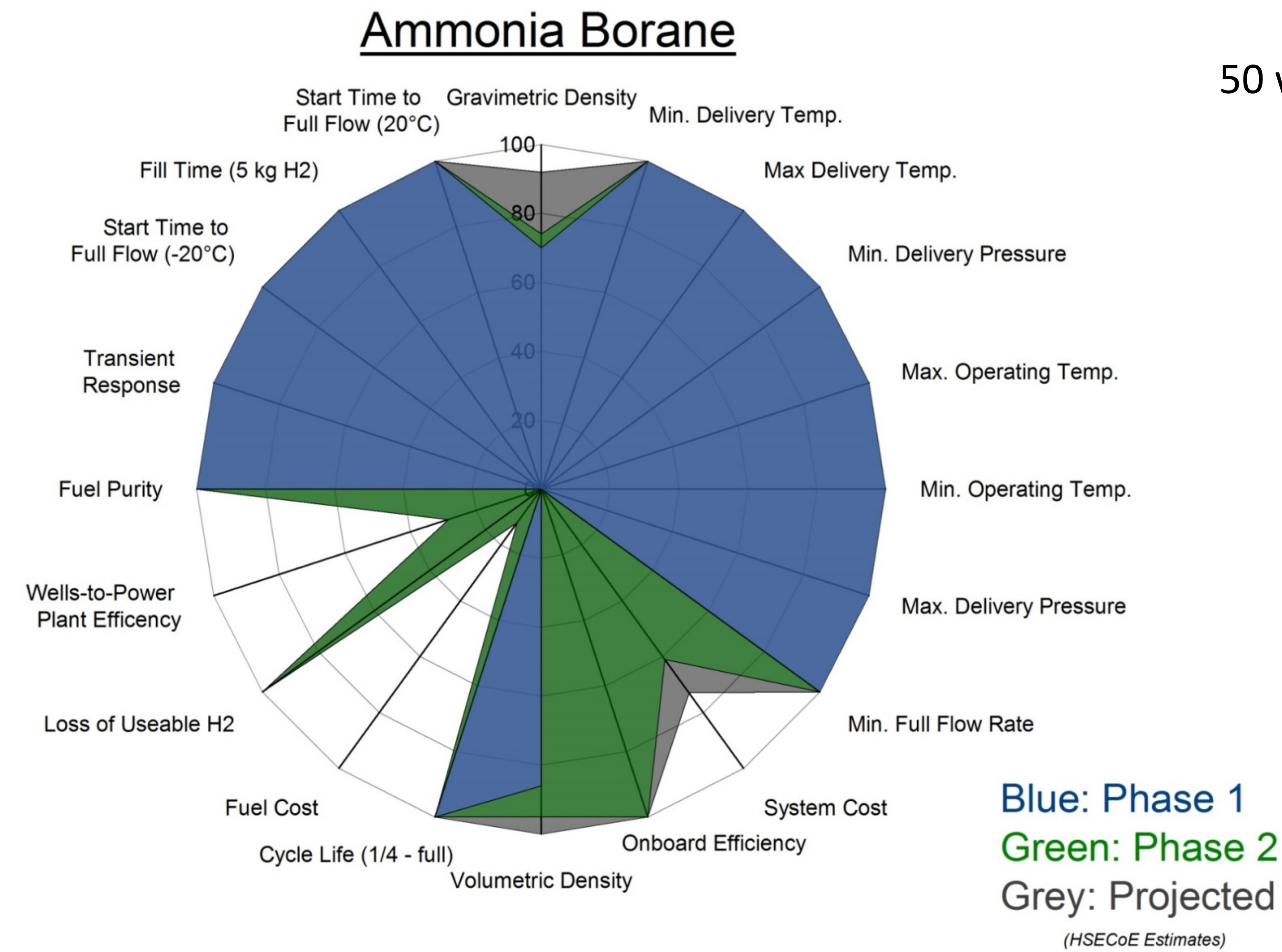
Relevance

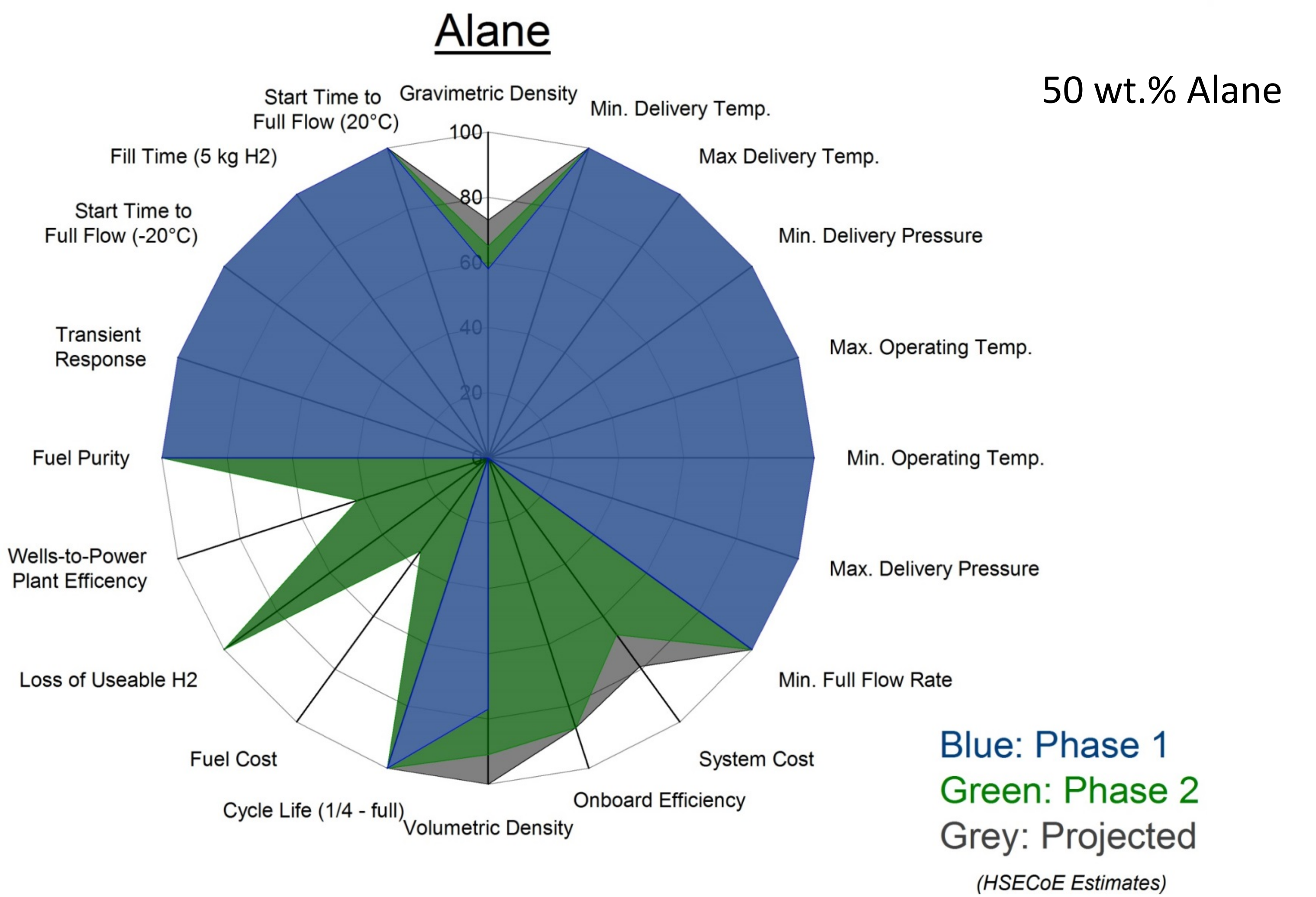
- Provide a validated modeling framework to the Energy Research Community (e.g., H2A)
- Provide an internally consistent operating envelop for materials comparison wrt
  - System/Component mass, volume, and cost
  - System performance
- Provide viable material properties that meet DOE 2017 system targets
- Identify and advance engineering solutions to address material-based non-idealities
- Identify, advance, and validate primary system level components

Project Status (DOE 2017 Targets)



- Projections meet 16 of the DOE 2017 system level targets
- Remaining challenges: *Fuel Cost, System Cost, WTPP, Gravimetric Density*

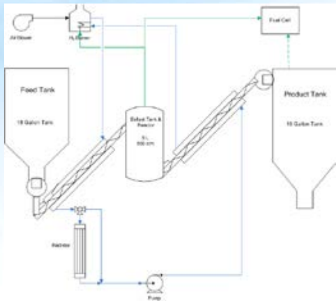
Project Status (DOE 2017 Targets)

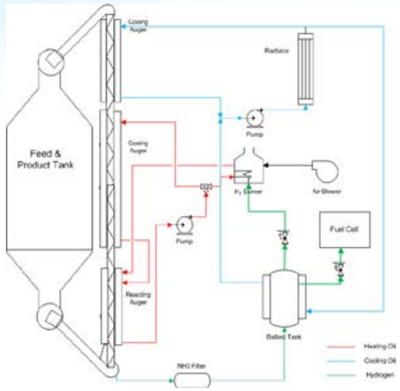


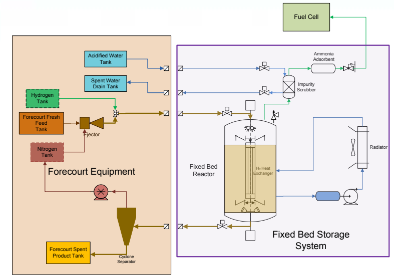
- Projections meet 15 of the DOE 2017 system level targets
- Remaining challenges: *Fuel Cost, System Cost, WTPP, TTW Gravimetric Density*

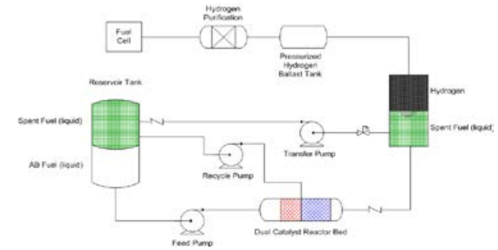
System Architect Section

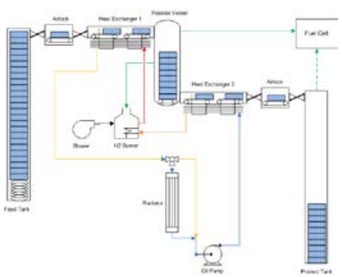
Accomplishments

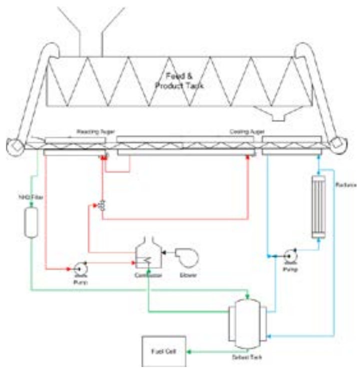


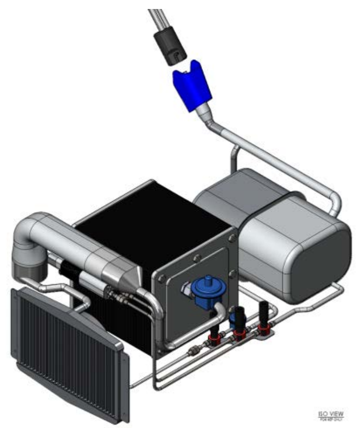


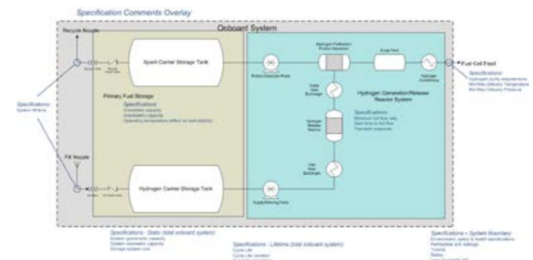


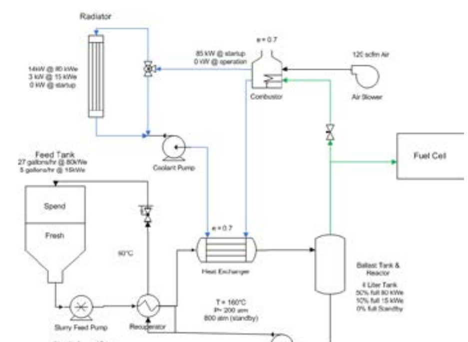












Other System Designs Not Shown Include:

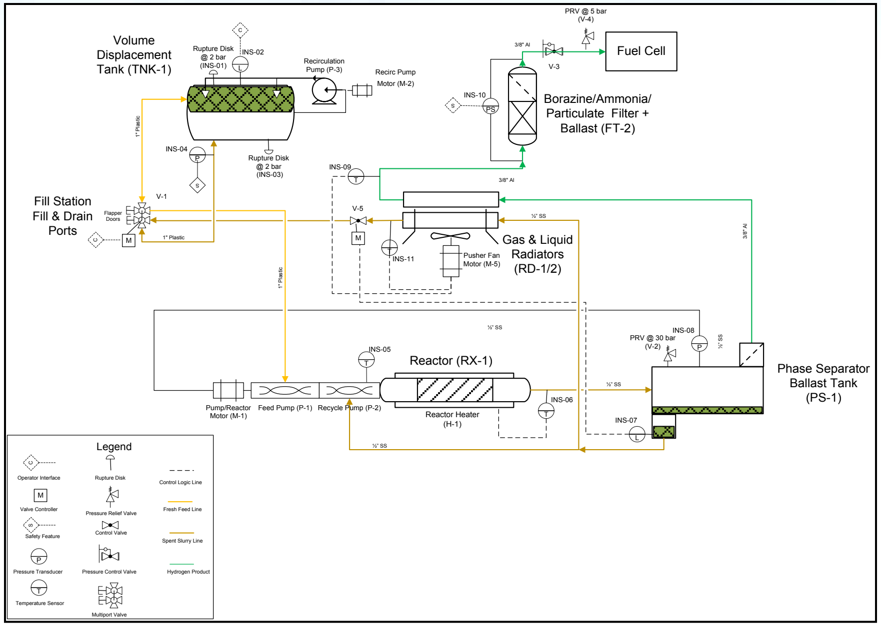
- CD Changer
- Rope
- Printer
- Gumball
- Fountain
- Heated Roller
- Soda Can
- Membrane Reactor
- 8 Track

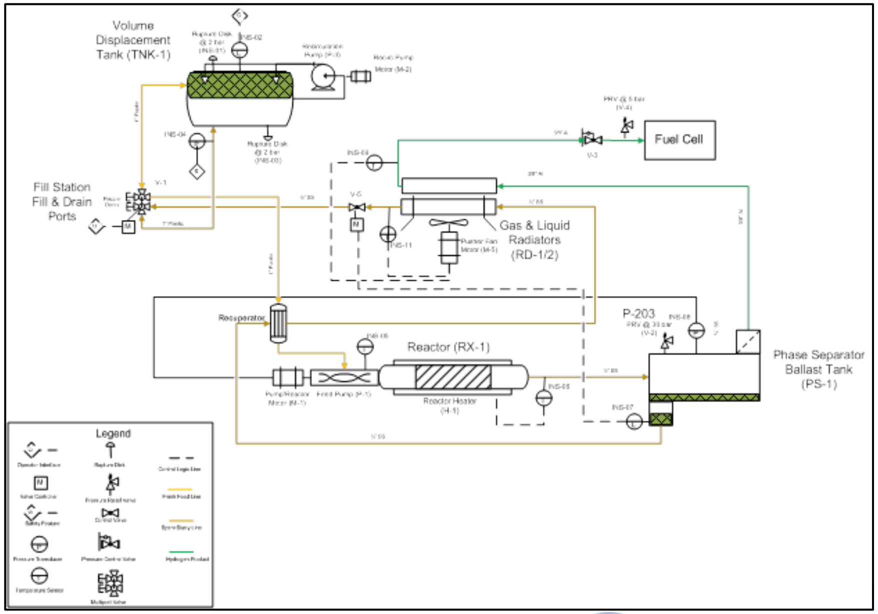
Numerous system designs developed for solid, liquid, and slurry phase media

Accomplishments

System Designs (exothermic & endothermic)

- Performance
- Mass
- Volume
- Balance of plant components
- Cost





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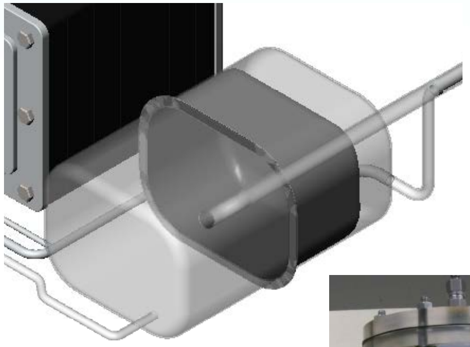
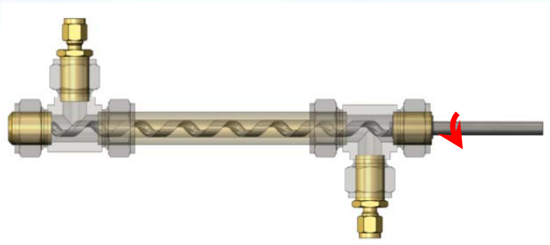
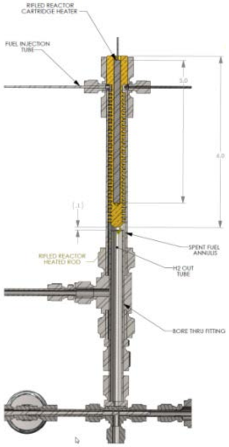
Accomplishments

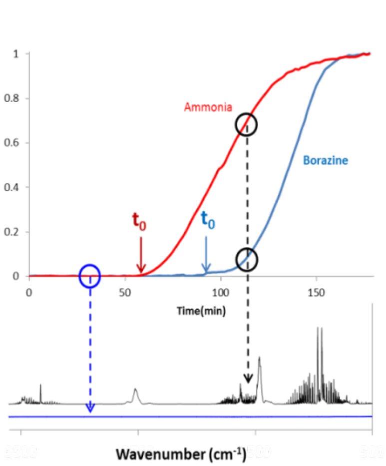
Designed, Built, & Validated System Components

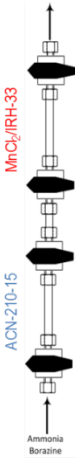
- Volume displacement tank
- Gas-liquid Separator
- Hydrogen Purification
- Fuel gauge sensor
- Reactors (slurry and liquid)

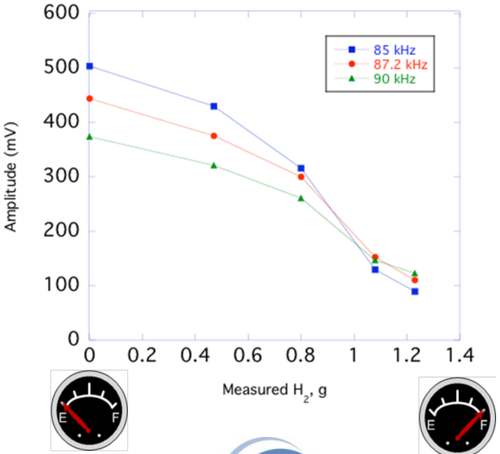


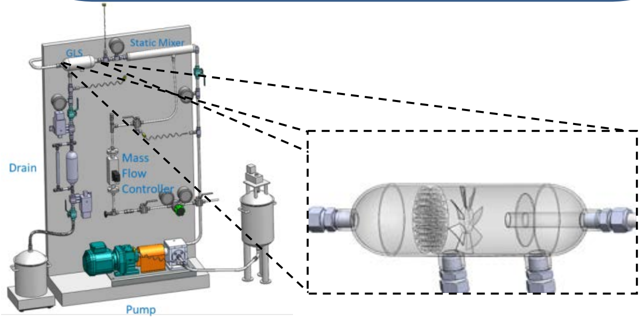










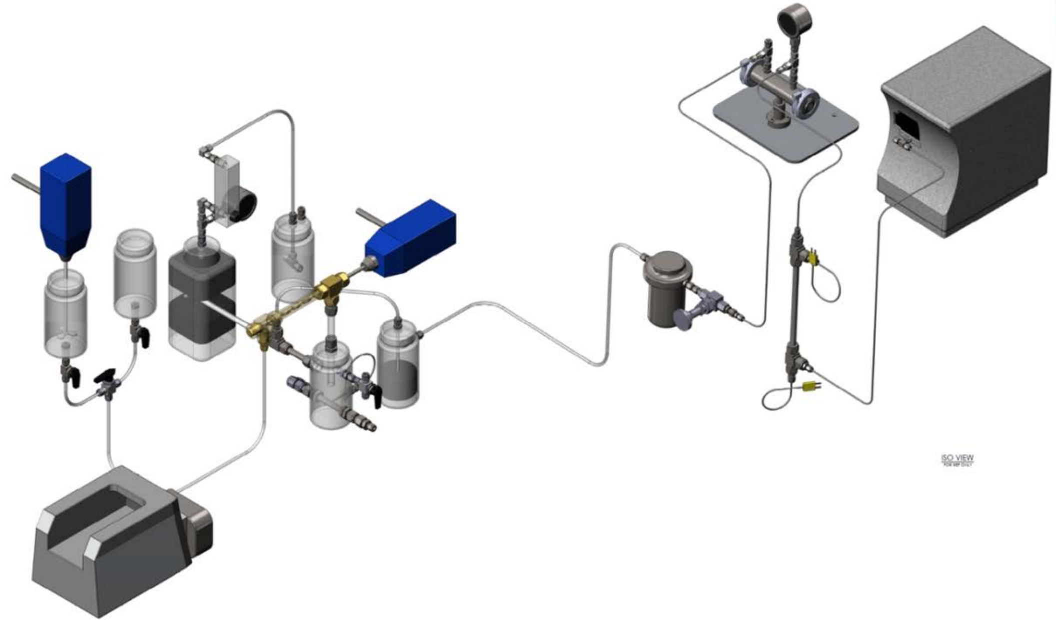


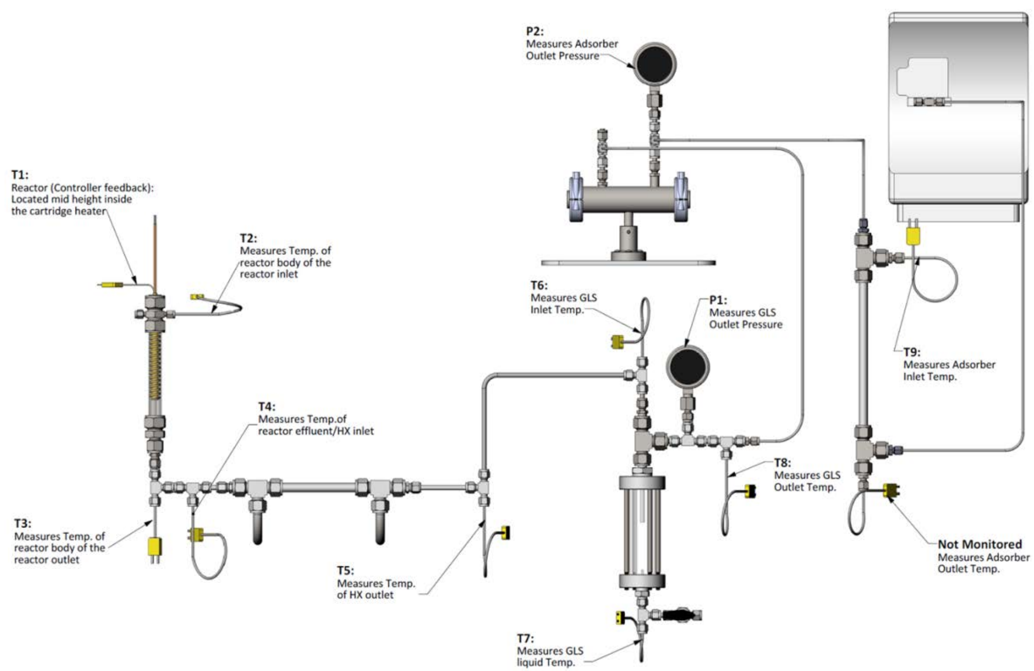
Gas/Liquid Separator

Accomplishments

Lab-scale Integrated systems

- Major system components
- Reaction characteristics
  - Alane slurry (6.5 wt.% H_2)
  - MPAB (3.9 wt.% H_2)
  - AB slurry (5 wt.% H_2)
- Fuel-cell grade hydrogen (99.99%)





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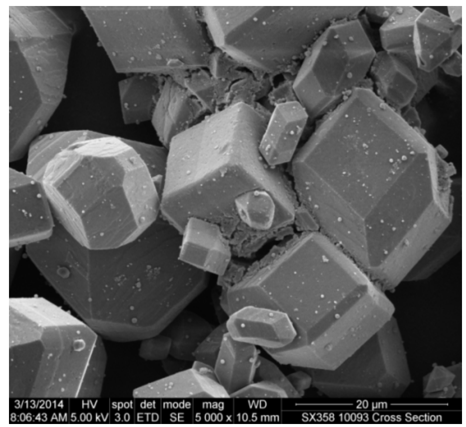
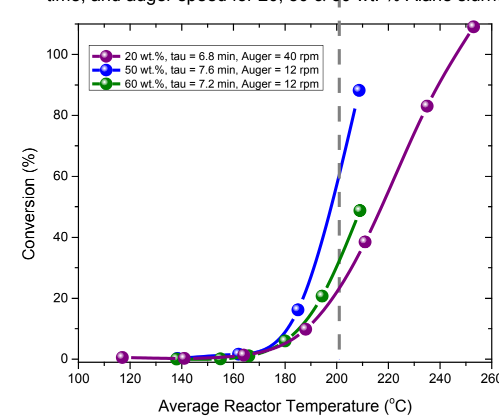
Accomplishments

Material Properties

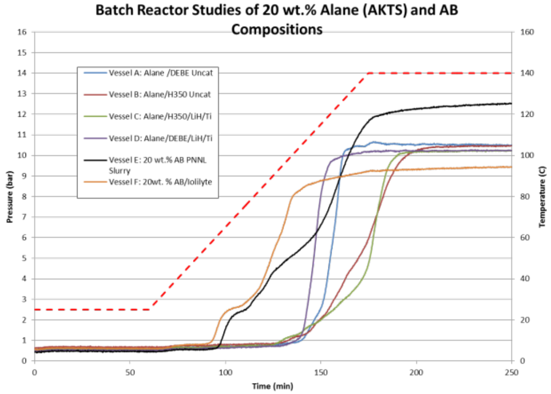
- Slurry development
- Novel CH liquid development
- Impurity quantification
- Kinetics

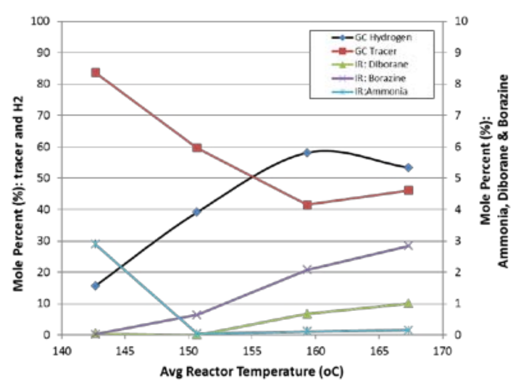


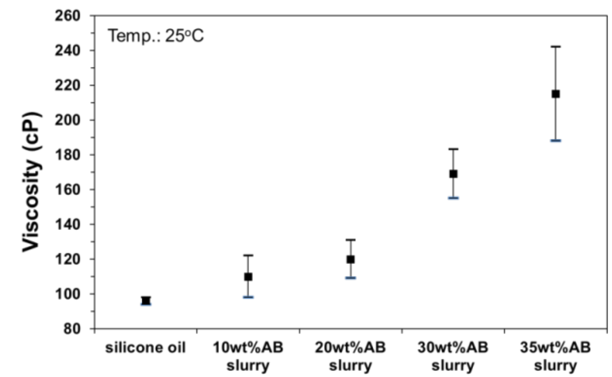
Alane conversion as a function of reactor temperature (C), space time, and auger speed for 20, 50 & 60 wt. % Alane slurries



Batch Reactor Studies of 20 wt.% Alane (AKTS) and AB Compositions



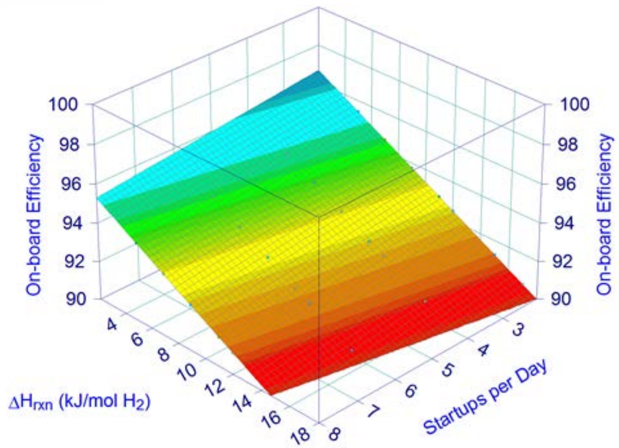


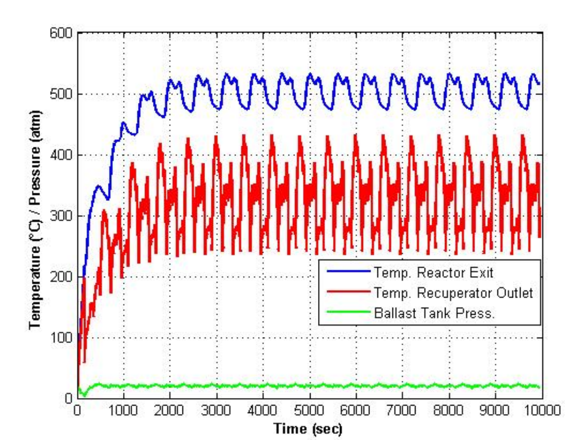


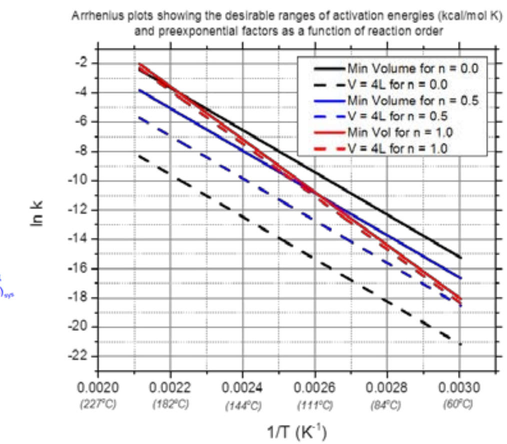
Accomplishments

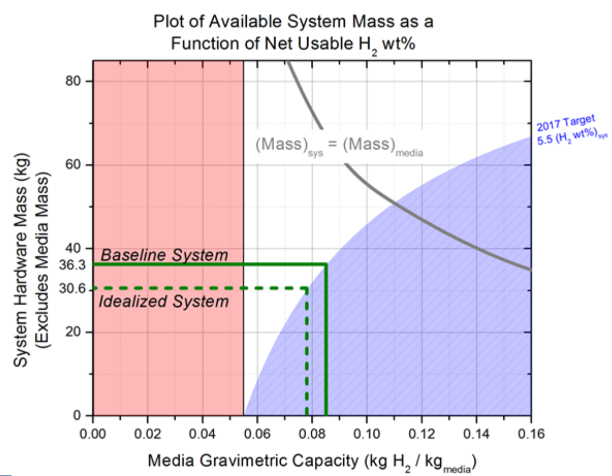
Modeling Tools

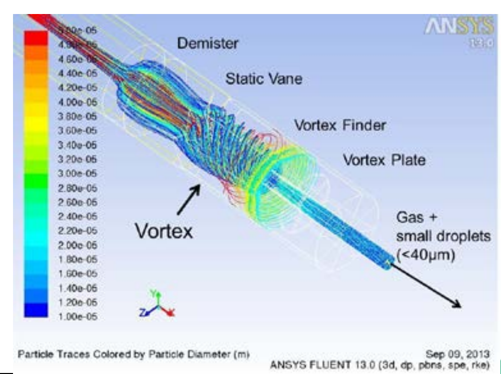
- System Models
  - Exothermic
  - Endothermic
  - Performance
  - Cost
- Material properties
  - Kinetics
  - Impurities
  - Regeneration efficiency
  - On-board efficiency
  - Heats of reaction
  - Gravimetric capacity
  - Volumetric capacity











Tools for:
- Engineering community
- Materials research community

Key Contributions of the Chemical Hydrogen Group

Three Years Ago:

- **NO**
  - ✗ System designs
  - ✗ System models
  - ✗ Efficiency analyses
  - ✗ Flow-through reactor experiments performed with AB or alane
  - ✗ Material property guidelines
  - ✗ Realizable media
- Solids and slurry handling concepts for onboard systems are technically challenging

Substantially increased our working knowledge on Chemical Hydrogen

- *System designs*
- *Material properties*
- *System models*
- *System components*

Current State:

- Developed material property guidelines
- Developed system models
- Validated all major system components
- Developed numerous designs
- Developed boilerplate system designs for endo- and exothermic media
- Performed WTT & TTW efficiency analyses
- Demonstrated viable reactor designs for fluid-phase media
- Developed preliminary system cost analyses
- Developed novel MPAB liquid
- Demonstrated lab-scale integrated chemical hydrogen storage system
- Developed novel fuel gauge sensor
- Solids and slurry handling concepts for onboard systems remain technically challenging

Chemical hydrogen storage material properties

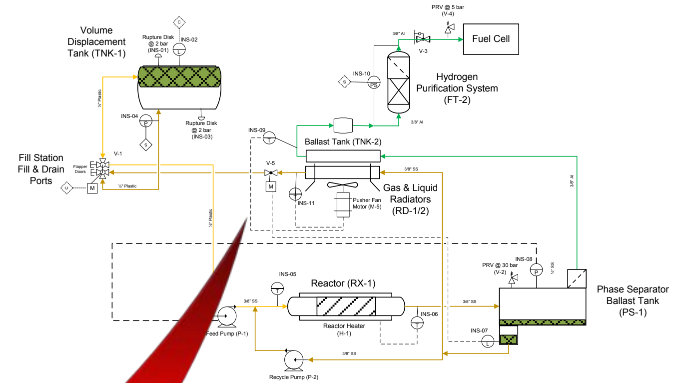
Objective:
Provide chemical hydrogen storage material property guidelines that will allow the overall system to meet the DOE 2017 performance targets

Approach:
1. Develop an integrated chemical hydrogen storage system for automotive applications
2. Develop a system model that predicts system performance using various drive cycles
3. Identify and size components that are material dependent
4. Determine material properties to meet DOE 2017 performance targets

Approach: Chemical Hydrogen Material Properties

Item #	Description	Material	Wt (kg)	Vol (L)
Tanks and Tubing				
TNK-1	Volume Displacement Tank	High Density Polyethylene	6.2	65.5
NA	Fill and Drain Lines	10 ft of 1/2" Plastic	0.17	0.38
NA	Low T and P Lines			
NA	High T and P Lines			
INS-01	Rupture Disk			
INS-02	Level Sensor for Volum Displacement Tank			
INS-03	Rupture Disk			
INS-04	Pressure sensor			
Feed Loop				
V-1	2 Multiport Valves with A			
V-1	Flapper Valves			
P-1	Feed Pump			
INS-05	Temperature sensor			
RX-1	Reactor			
H-1	Reactor Heater			
INS-06	Temperature sensor			
INS-07	Level Sensor for P/S			
Recycle Loop				
P-2	Recycle Pump			

Item #	Description	Material	Wt (kg)	Vol (L)
Return Loop				
PS-1	Gas Liquid Separator	347/347L SS	3.2	3.7
INS-08	Pressure sensor	316L SS	0.14	0.001
V-2	Pressure Relief Valve		0.3	0.1
RD-2	Liquid Radiator	304 SS	2.08	2.9
RD-2	Liquid Radiator Header	304 SS	0.16	0.06
M-5	Liquid Radiator Fan Ultra Thin Line 12V Electric Fan (Puller)	Nylon	1	5.9
INS-11	Temperature sensor		0.1	0.02
V-5	Control Valve	Brass	1.7	0.75
Hydrogen Discharge				
FT-1	Coalescing Filter	SS	1.2	0.34
RD-2	Gas Radiator	304 SS	0.3	0.3
RD-2	Gas Radiator Header	304 SS	0.16	0.03
INS-09	Temperature sensor		0.1	0.02
INS-10	Pressure Switch		0.1	0.001
FT-2	H2 Clean-Up System		3.2	4
TNK-2	Additional Ballast Tank	Aluminum, L/D =4 , SF = 1.5	2.6	15
FT-4	Particulate Filter	SS	1.2	0.34
V-3	Pressure Regulator Gas		0.6	0.5
V-4	Pressure Relief Valve		0.6	0.16



Systems Components

DOE 2017 System

Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
• Operating ambient temperature	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full)	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
• System fill time (5 kg)	min (kg H_2/min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C)	s	5	5	5
• Start time to full flow (-20°C)	s	15	15	15
• Transient response 10%-90% and 90% - 0%	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage)	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety:				
• Permeation & leakage	Scc/h	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H_2	(g/h)/kg H_2 stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh/MJ; 33.3 kWh/kg H_2; 1 kg H_2 ≈ 1 gal gasoline equivalent.

Parameter	Units	Rang
Minimum Material capacity (liquids)	g $_{H2}$ / g $_{material}$	~ 0.078
Minimum Material capacity (solutions)	g $_{H2}$ / g $_{material}$	~ 0.0
Minimum Material capacity (slurries)	g $_{H2}$ / g $_{material}$	~ 0
Endothermic Heat of Reaction	kJ / mol H_2	
Exothermic Heat of Reaction	kJ / mol H_2	
Maximum Reactor Outlet Temperature	°C	
Impurities Concentration	ppm	No *a priori* esti… can be quantified
Media H_2 Density	kg H_2 / L	≥ 0.07
Regeneration Efficiency	%	≥ 66.6%
Viscosity	cP	≤ 1500

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Accomplishments

Parameter	Units	Range*
Minimum Material capacity (liquids)	$g_{H2} / g_{material}$	~ 0.078 (*0.085*)†
Minimum Material capacity (solutions)	$g_{H2} / g_{material}$	~ 0.098 (*0.106*) †
Minimum Material capacity (slurries)	$g_{H2} / g_{material}$	~ 0.112 (*0.121*) †
Endothermic Heat of Reaction	kJ / mol H_2	≤ +17 (*15*) †
Exothermic Heat of Reaction	kJ / mol H_2	≤ -27
Maximum Reactor Outlet Temperature	°C	250
Impurities Concentration	ppm	No *a priori* estimates can be quantified
Media H_2 Density	kg H_2 / L	≥ 0.07
Regeneration Efficiency	%	≥ 66.6%
Viscosity	cP	≤ 1500

** (a) parameter values are based on a specific system design and component performance with fixed masses and volumes (b) values outside these ranges do not imply that a material is not capable of meeting the system performance targets (c) the material property ranges are subject to change as new or alternate technologies and/or new system designs are developed (d) the minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized*

† values outside of parentheses are the values that correlate to the idealized system design (i.e., 30.6 kg) and the values in parentheses are those that correlate to the base system design (36.3 kg)

Accomplishments

Arrhenius Parameters	Units	Range*
Kinetics: Activation Energy	kJ / mol	117-150
Kinetics: Preexponential Factor		$4 \times 10^{9} – 1 \times 10^{16}$

Reaction Order (n)	Minimum Temperature (°C)
0.13	100
0.5	125
1	175
2	300

Developed material property guidelines to foster materials development

** (a) parameter values are based on a specific system design and component performance with fixed masses and volumes (b) values outside these ranges do not imply that a material is not capable of meeting the system performance targets (c) the material property ranges are subject to change as new or alternate technologies and/or new system designs are developed (d) the minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized*

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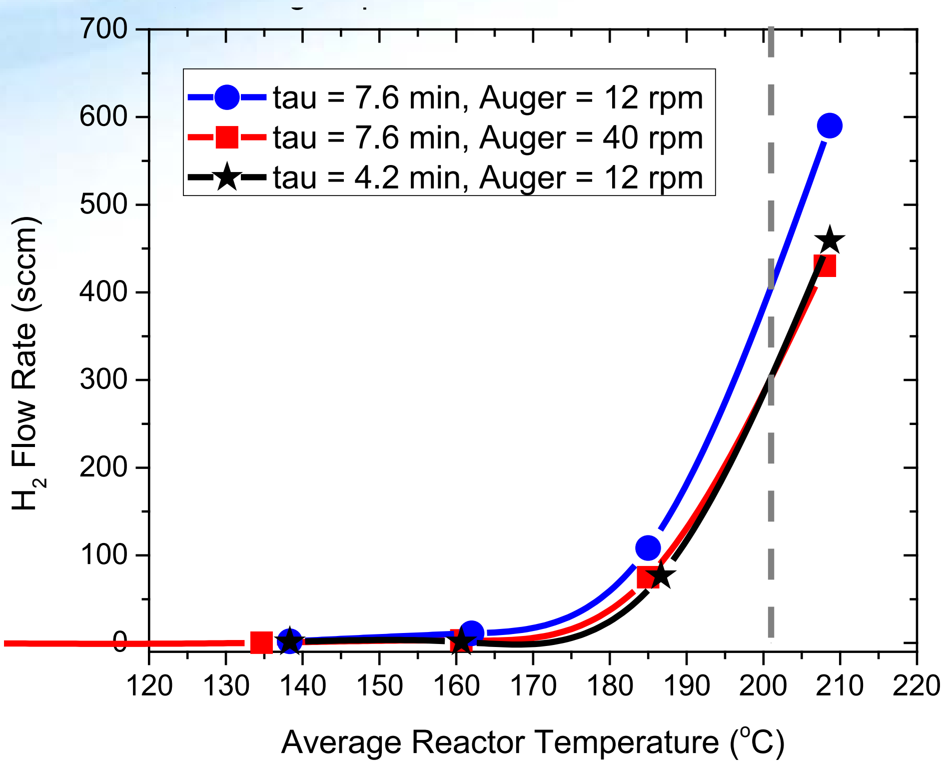
Mechanically mediated reactive transport of slurry compositions

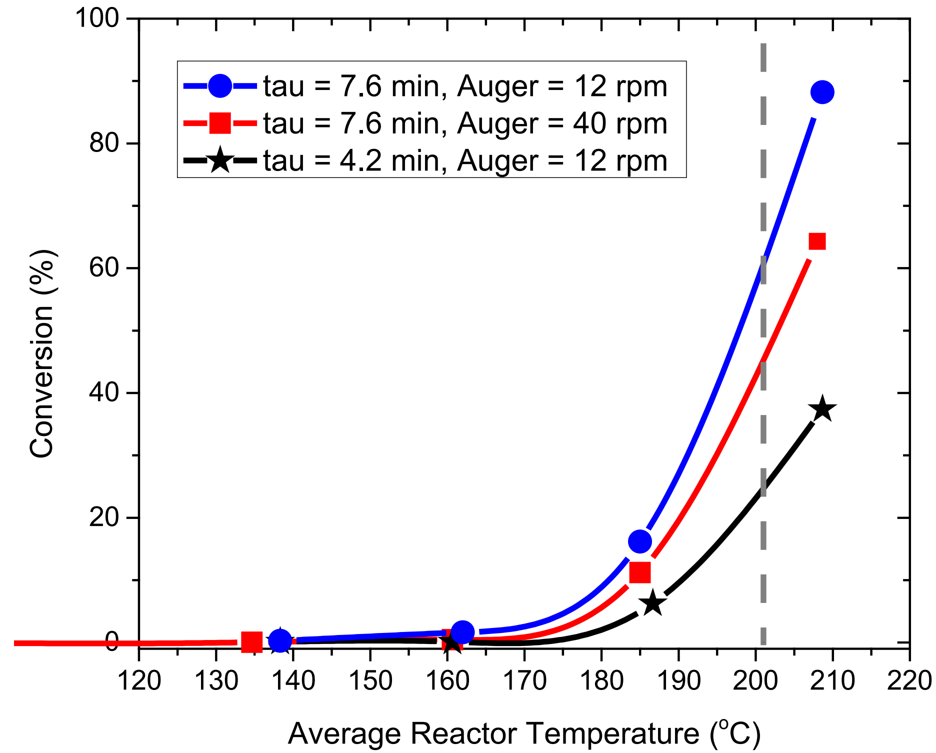
Objectives:

1. Design and validate auger reactor for slurries
2. Determine flow through reactor performance with slurries
3. Determine reaction characteristics of alane slurries
   - Alane loadings (50-65 wt. %)
   - Liquid carrier (Si oil, tetraglyme, pump oil)
   - Dopants (LiH and Ti)

Approach: To design, build, and validate auger reactor for slurry-phase chemical hydrogen storage media with enhanced gas-liquid separation and mitigating strategies for reactor fouling and reactor slugging

50 wt.% Alane/Si Oil/Triton X-15

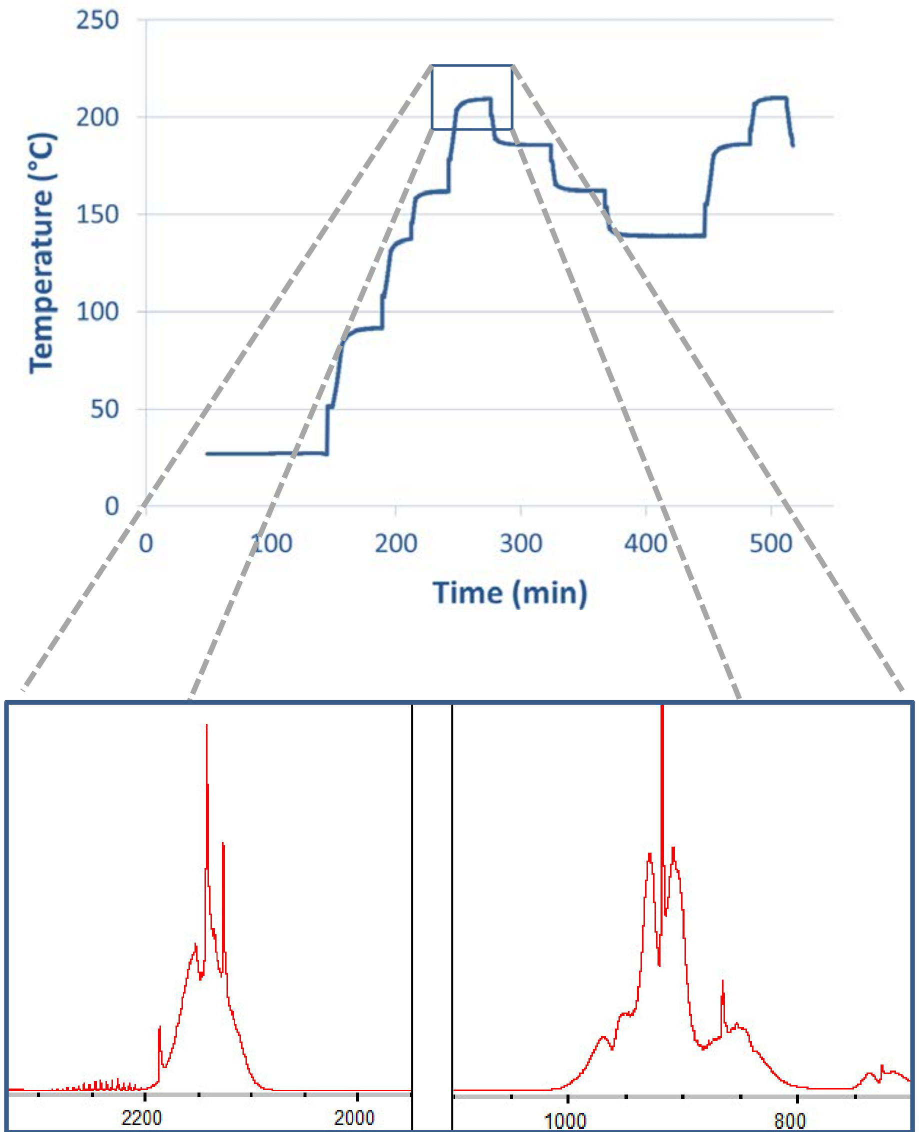


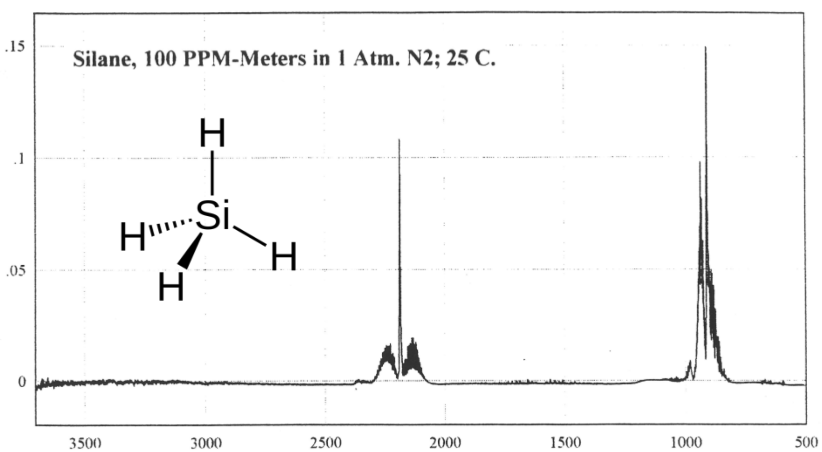


- Successfully demonstrated auger reactor with 50 wt.% alane slurry and high conversion
- No reactor clogging or fouling observed

50 wt.% Alane/Si Oil/Triton X-15

- Si-H IR transitions for temperatures > 200 °C
- Partial vaporization of silicon oil carrier evidenced by cloud formation around 200 °C
- Silicon based carriers resulted in chemical incompatibilities with alane for T > 200°C





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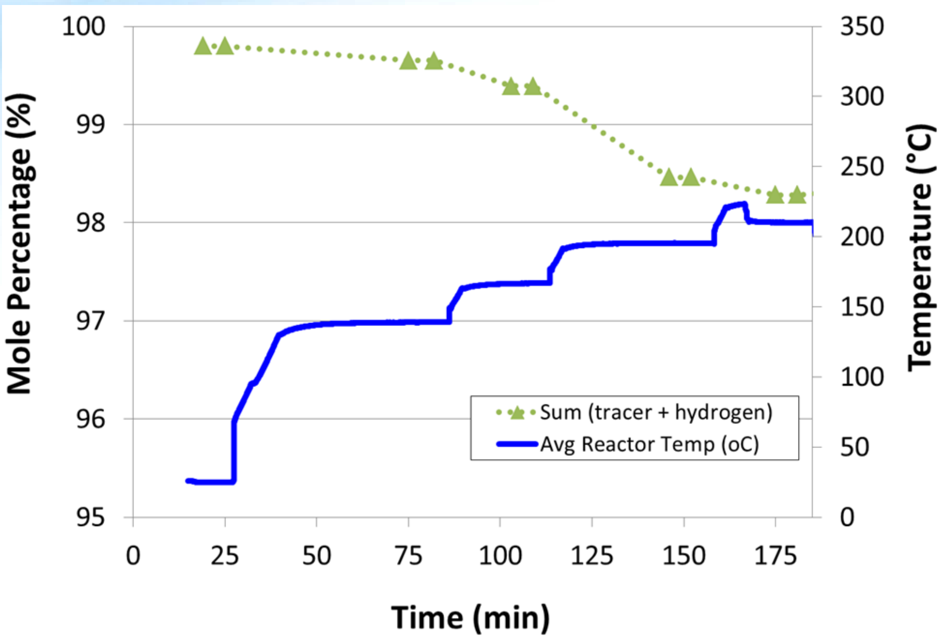
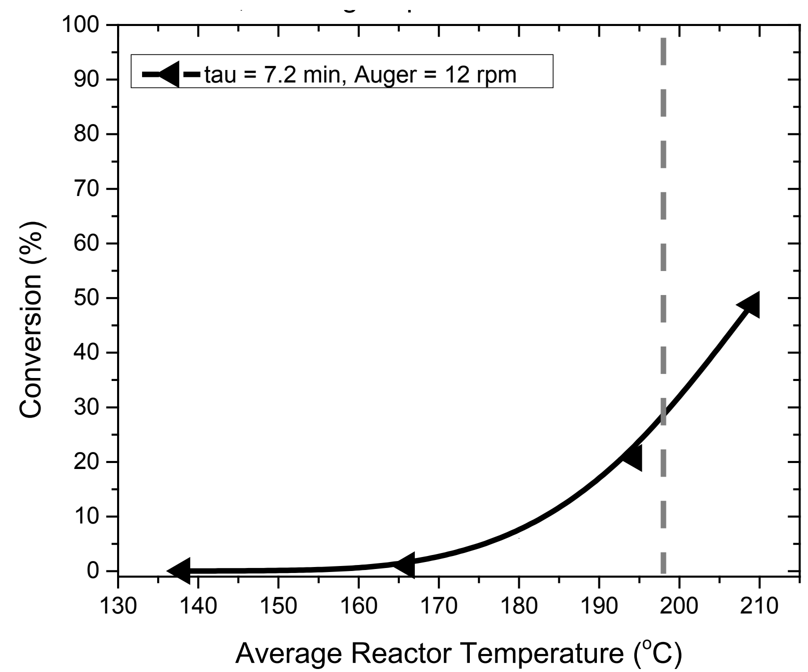
60 wt.% Alane/Mechanical Pump Fluid (MPF)





- Successfully demonstrated 60 wt.% slurry
- Mechanical Pump Fluid (non-silicon based) shown to eliminate the production of silane-like impurities
- Hydrogen fuel quality is around 98% (pre-H_2 purification) and > 99.9% (post-H_2 purification)
- Unidentified impurity

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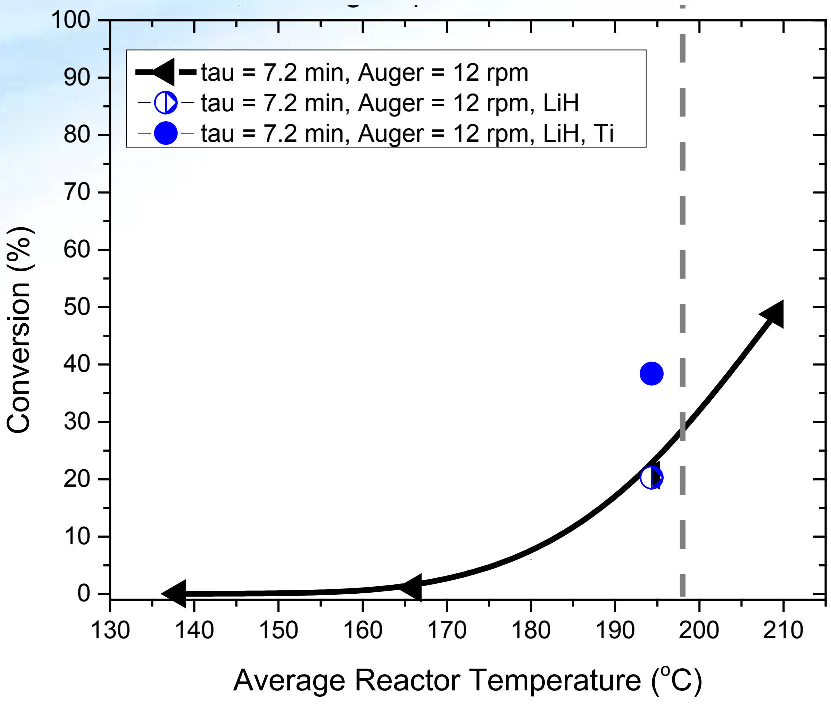
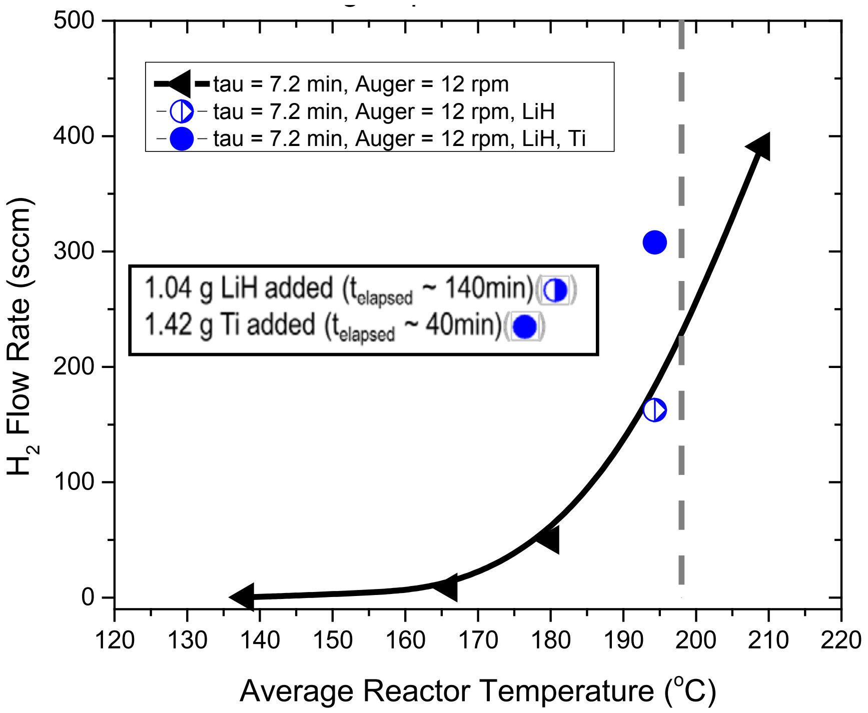
60 wt.% Alane/Mechanical Pump Fluid/LiH/Ti

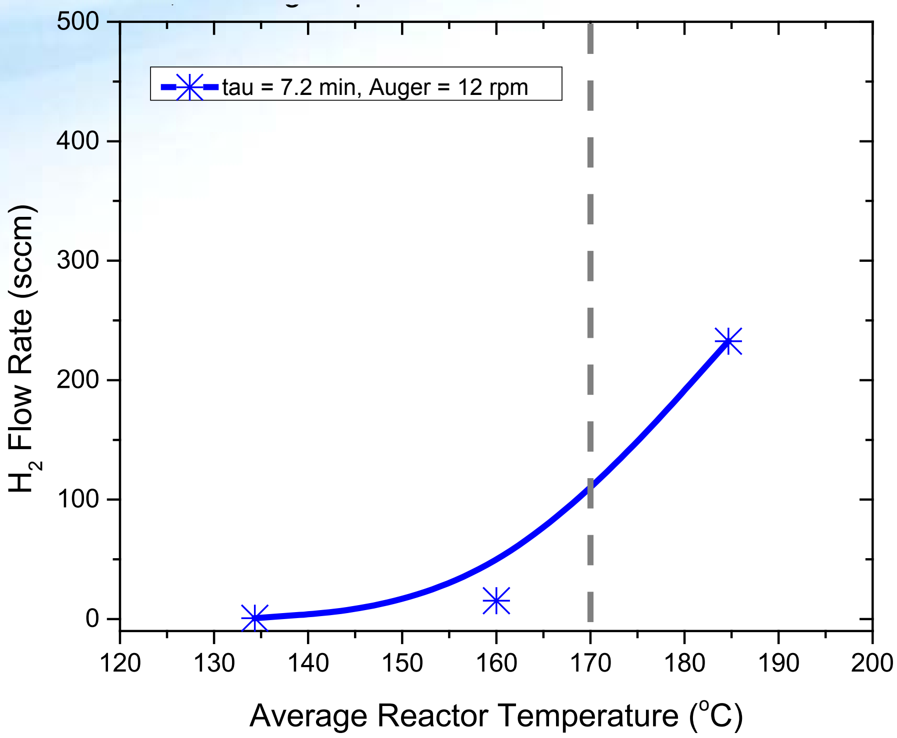


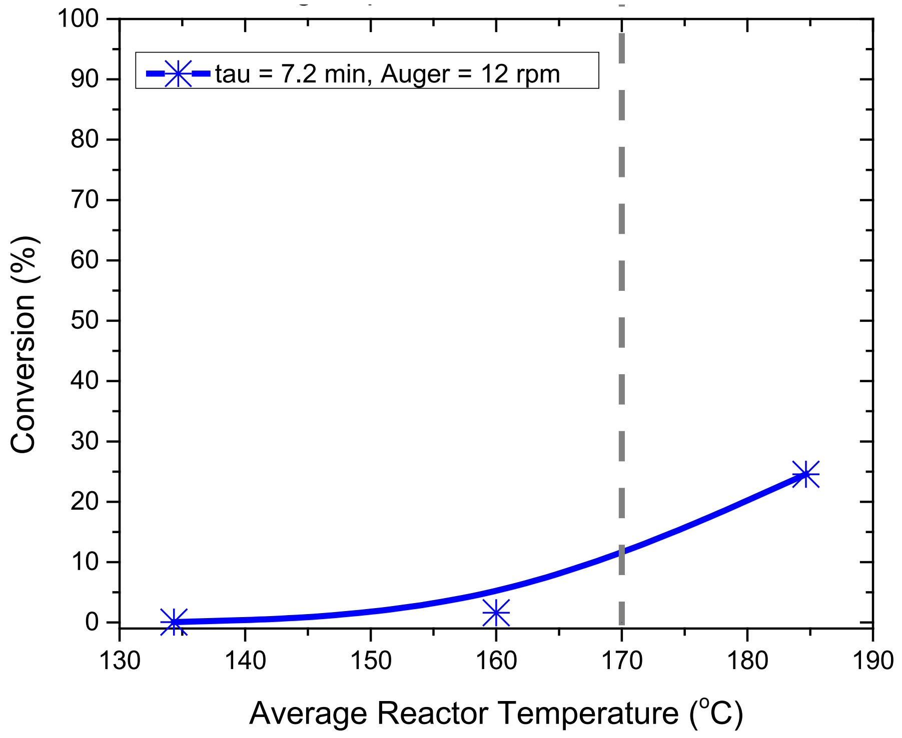


– LiH alone did not promote alane dehydrogenation
– LiH + Ti nearly doubled the conversion rate
– Dopants did not impact reaction selective/impurity production

UNCLASSIFIED

65 wt.% Alane/Tetraglyme (TG)/Triton X-15





Choice of slurry carrier is critical for reactor operability and durability

- Reactor plugged within 1.5 hrs–*no gas or liquid flow*
- Flash vaporization of carrier resulted in solids buildup

2013 AMR Reviewer Comments

- It is worth trying MPAB or other liquid hydrogen carriers as a slurry agent for alane or AB
  - ➢ We have tried using MPAB as a hydrogen bearing slurry carrier for AB, but the composition is unstable and begins reacting immediately upon mixing.

- Other slurry media should be considered for alane. Silicon oil is a reasonable first choice, but other liquids show much better kinetics.
  - ➢ Yes, we have demonstrated that the choice carrier impacts alane dehydrogenation kinetics (i.e., tetraglyme, DEGB, H350, pump oil….). The choice of carrier cannot be chosen solely based on kinetics—boiling point, thermal stability and chemical stability are also important.

- The work on AB should be curtailed and the more generally relevant work on the representative liquid material should be expanded.
  - ➢ Agree: Our plans were to extend our work in Phase 3 to include alane slurries, MPAB, and potentially $LiAlH_4$, but the chemical hydrogen work has been discontinued.

Key Takeaways

- Unified material properties with system designs, system components, system performance and system models
- Developed a set of <u>material</u> property guidelines expected to meet the DOE 2017 <u>system</u> targets
- Choice of carrier is a critical element for system operability and durability for both solution phase and slurry phase chemical hydrogen storage media
  - Boiling point alone cannot be the decision metric for carrier or solvent choice
  - Solvent/carrier thermal stability within the operating temperature range
  - Solvent/carrier must be chemically inert with storage media over the operating temperature range
  - Reactor operating temperatures greater than 0.7 of the solvent/carrier boiling point promote reactor fouling because of the increased rate of carrier evaporation
- Slurry phase reactors are viable but at the expense increased system: mass, volume, efficiency, cost, complexity, and maintenance

  ………and most likely a decrease in the hydrogen gravimetric capacity of the slurry
- Neat liquids with operating temperatures greater than 0.7 of its boiling point may require larger reaction volumes with recycle due to limited single-pass conversions

  ………and depending on the reaction order may result in limited overall conversion

Future Work

- Wrap up Chemical Hydrogen Work
    - Finalize Model Development
    - Deploy Models
    - DOE Final Report
    - Peer-Reviewed Manuscripts

Collaborations

External Collaborators	Effort	Contact
Chemical Hydrogen Storage Researchers	Materials Research	J. Wegrzyn (BNL)
		T. Baker (U. Ottawa)
		B. Davis (LANL)
H_2 Production & Delivery Tech Team	WTT Analyses	M. Pastor (DOE)
		B. James
LANL Fuel Cell Team	General Guidance Fuel Cell Impurities	T. Rockward (LANL)
		R. Borup (LANL)
H_2 Safety Panel	General Guidance/Concerns	S. Weiner
SSAWG	Technical Collaboration	G. Ordaz (DOE)
H_2 Storage Tech Team	General Guidance	Ned Stetson (DOE)
Argonne National Laboratory	Independent Analyses	R. Ahluwalia

HSECoE Collaborators	Effort	Contact
UTRC	Ammonia Scrubbing	B. van Hassel
	Simulink Modeling	J. Miguel Pasini
	Gas-Liquid Separator	Randy McGee
PNNL	MOR	E. Ronnebro
	System Modeling	K. Brooks
	BOP	K. Simmons
NREL	Vehicle Modeling	M. Thornton
SRNL	Slurry Mixing	David Tamburello
Ford	FMEA	Mike Veenstra

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Ned Stetson and Jesse Adams