Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Chemical Hydrogen Rate Modeling, Validation, and System Demonstration

LANL Team

Troy A. Semelsberger, Ben L. Davis, Brian D.Rekken, Biswajit Paik, and Jose I. Tafoya,

DOE Fuel Cell Technologies Program Annual Merit Review,
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program
Washington, DC May 13-17, 2013
Technology Team Lead: Ned Stetson

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The Institute for Hydrogen and Fuel Cell Research

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Project ID: st007_semelsberger_2013_O

LANL Project Overview

Timeline

- Project Start Date: Feb FY09
- Project End Date: FY14
- Percent Complete: 65%

Budget

- Total Project Funding: $4.7M
  - DOE Share: $4.7M
- Funding:
  - 2012: $900K
  - 2013: $880K

Barriers

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

Project Timeline

Phase 1									Phase 2						Phase 3					
2009			2010				2011		2011		2012				2013				2014	
Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2

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 component scaling as a function of chemical hydrogen storage media and application
- Provide materials operating envelop required to meet DOE 2017 targets
- Identify and advance engineering solutions to address material-based non-idealities
- Identify, advance, and validate primary system level components

System Architect Section

Overall HSECoE Objectives

1. Validate chemical hydrogen storage system model
2. Determine viable chemical hydrogen storage material properties
3. Develop and demonstrate “advanced” (non-prototypical) engineering concepts

HSECoE Phase 1-3 Objectives

Phase 1:

- Identify Essential System Components
- Develop Preliminary System Designs & Model Framework

Phase 2:

- Validate System Components
- Refine System Models and System Designs

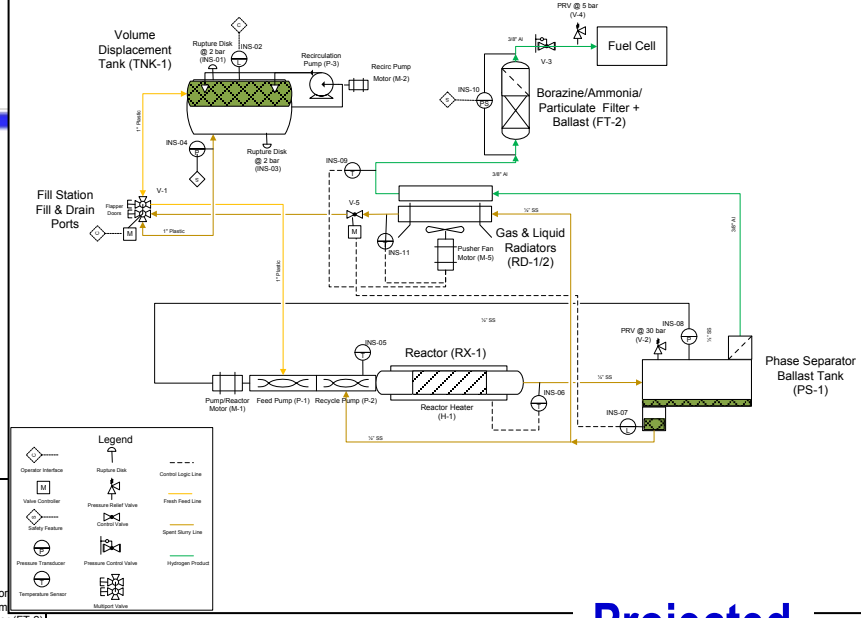
Phase 3:

- Validate Integrated System Components
- Validate and Refine System Level Models and System Design

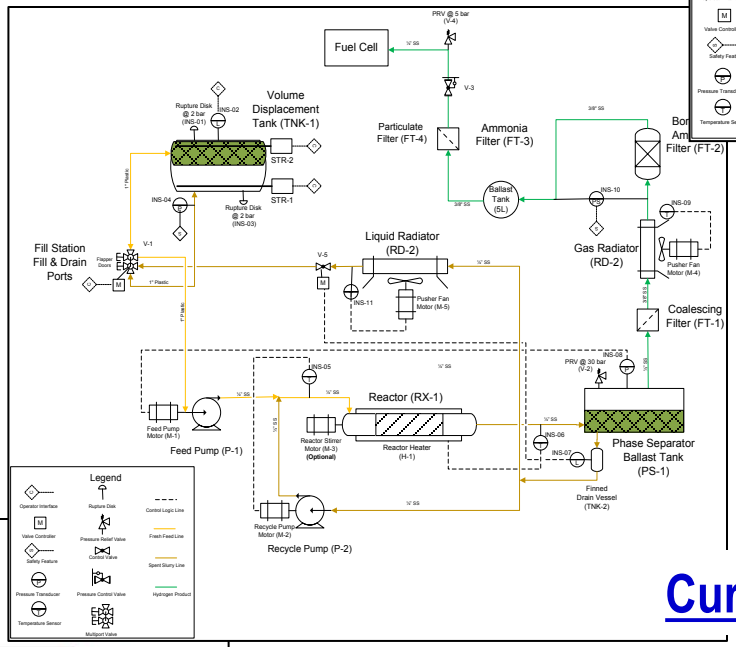
Ammonia Borane System Designs

50 wt. % Slurry-Phase AB

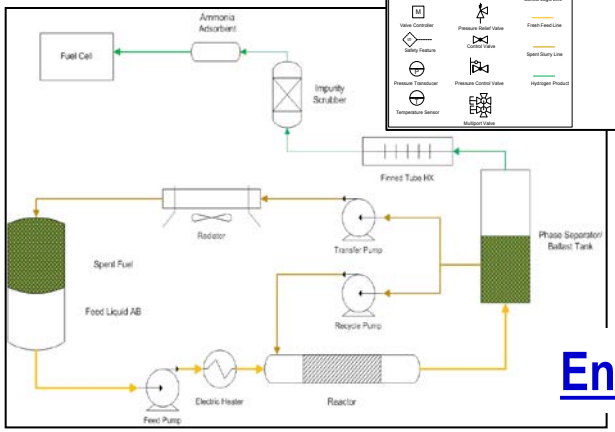
Exothermic Model



Projected



Current



End of Phase 1

Primary Unit Operations

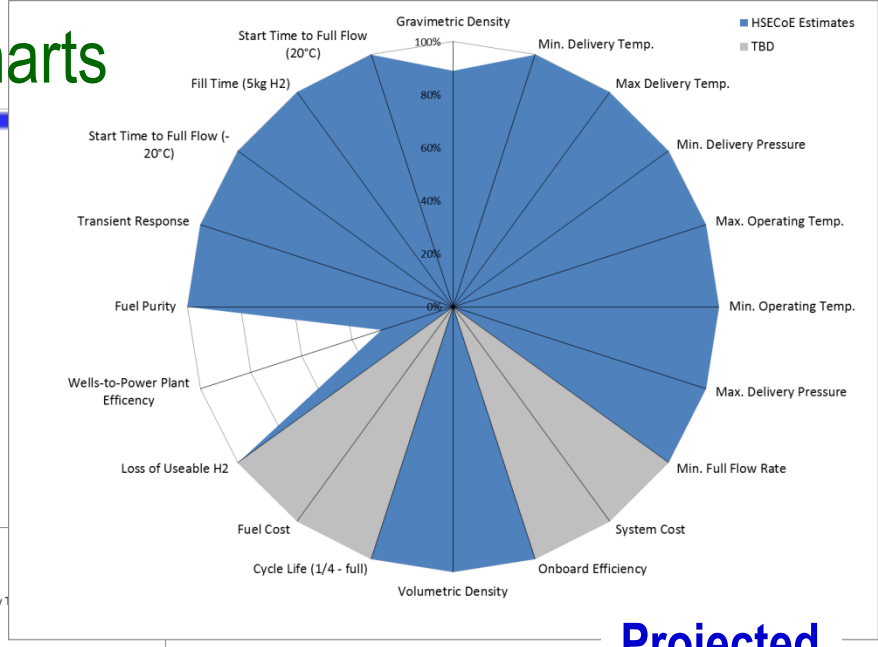
- Volume Displacement Tank
- Reactor
- Gas-Liquid Separator
- Ballast Tank
- Heat Exchangers
- H_2 Purification
- Recycle Loop

HSECoE

50 wt.% Ammonia Borane Spider Charts

50 wt. % Fluid-Phase Ammonia Borane

Exothermic Model



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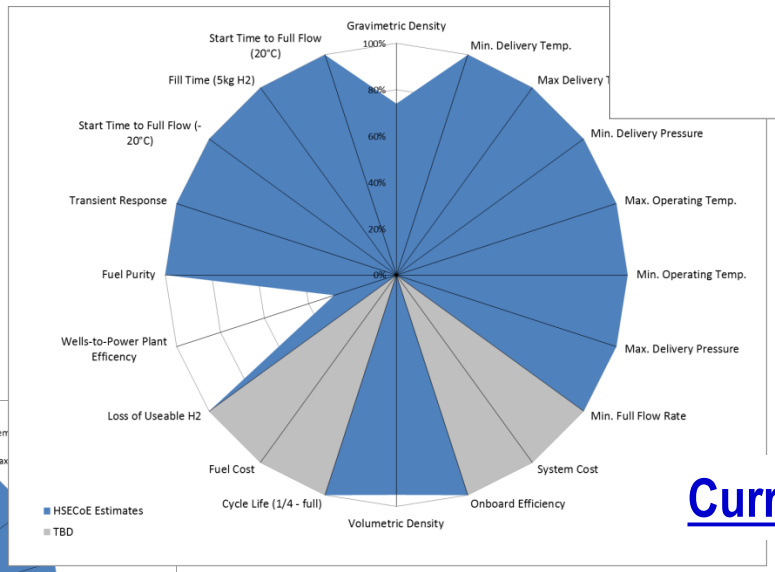

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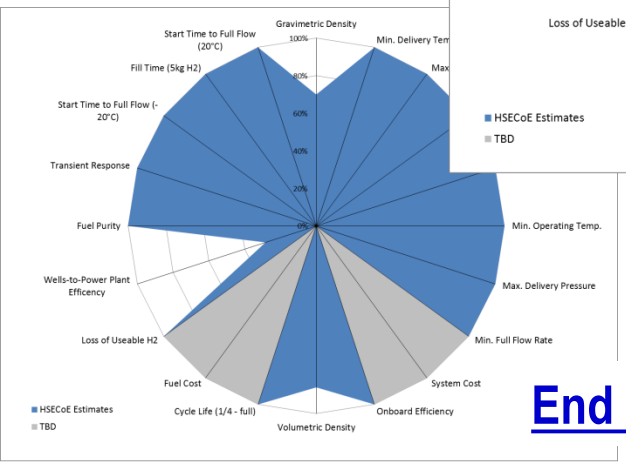

End of Phase 1

FOCUS AREAS

System Mass
System Volume

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HSECoE

Projected Improvements for Ammonia Borane Slurry System

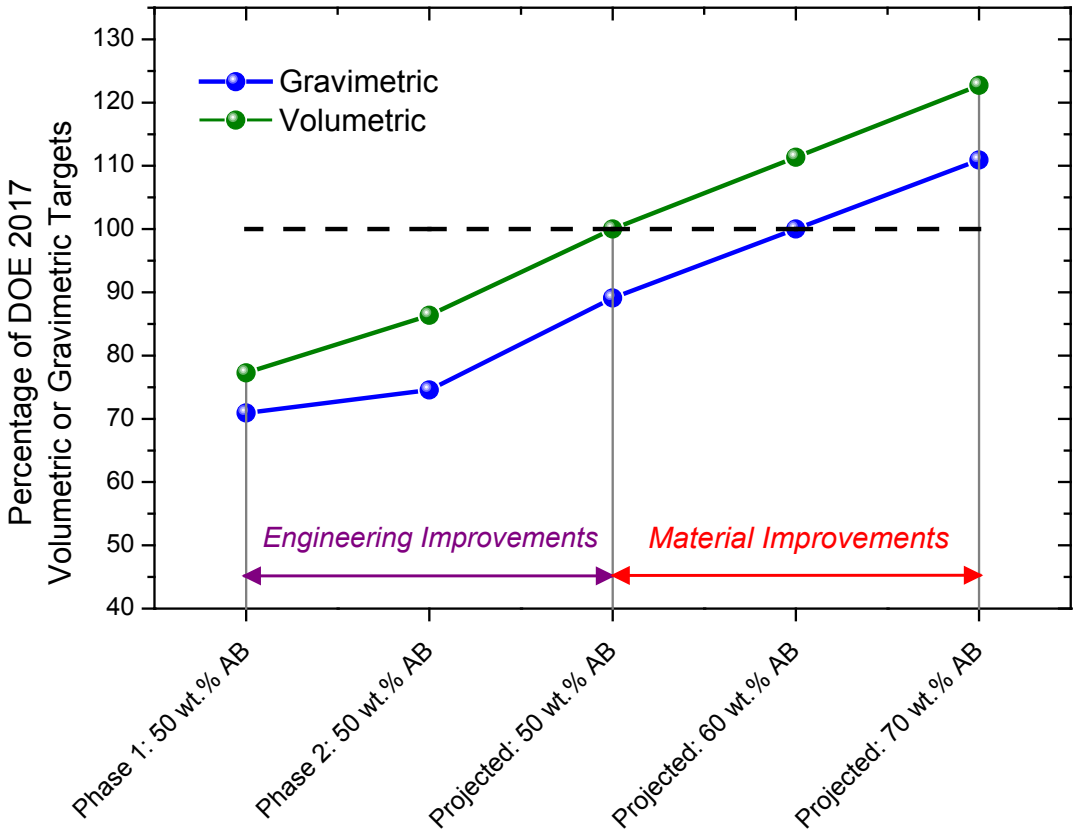
Engineering Improvements

Phase 1 to Phase 2 (Current)

- Phase 2 Component Validation Results
- Higher fidelity System Models and System Designs

Phase 2 (Current) to Projected

- Component Integration
- Component Performance Enhancements



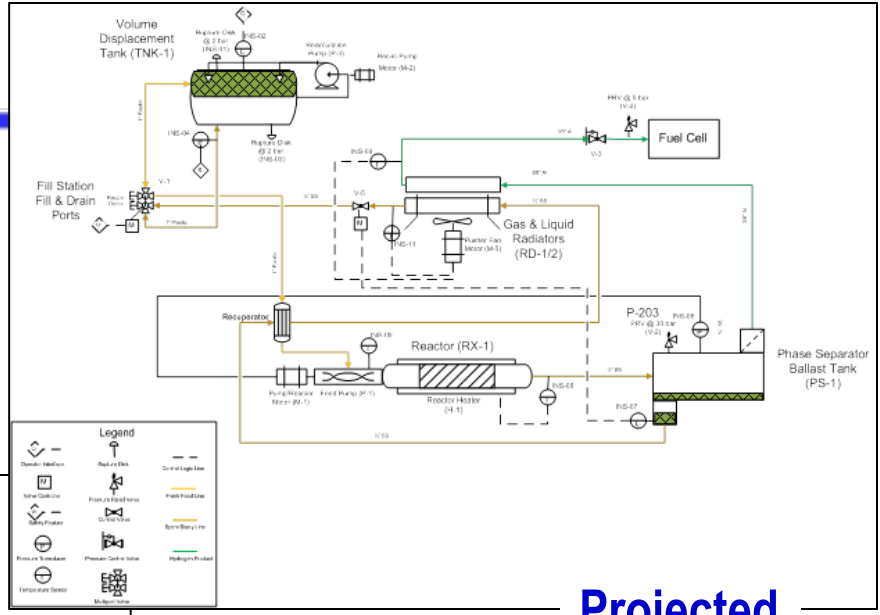
Material Improvements

60 wt.% AB slurry (~ 8.7 wt. % H_2) will meet both the DOE 2017 gravimetric and volumetric targets

Alane Slurry System Designs

50 wt. % Alane Slurry

Endothermic Model



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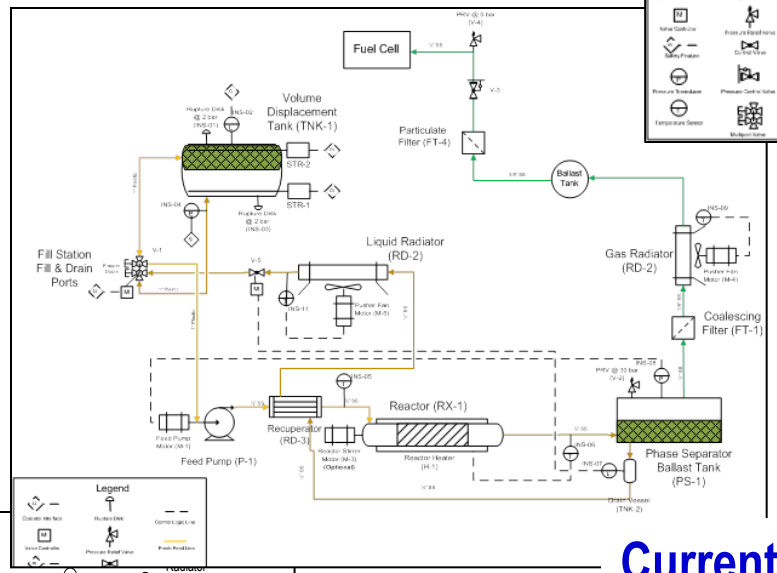
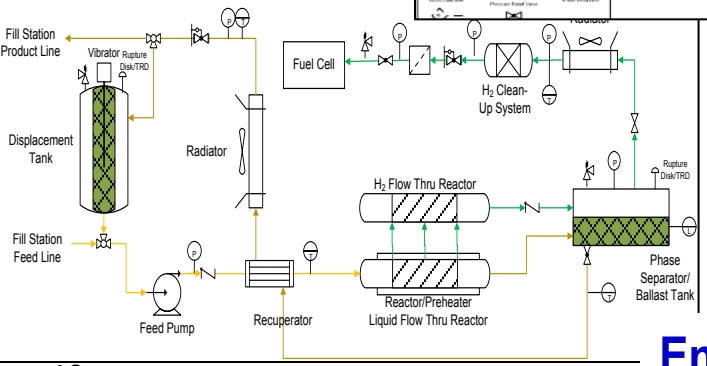


Current



End of Phase 1

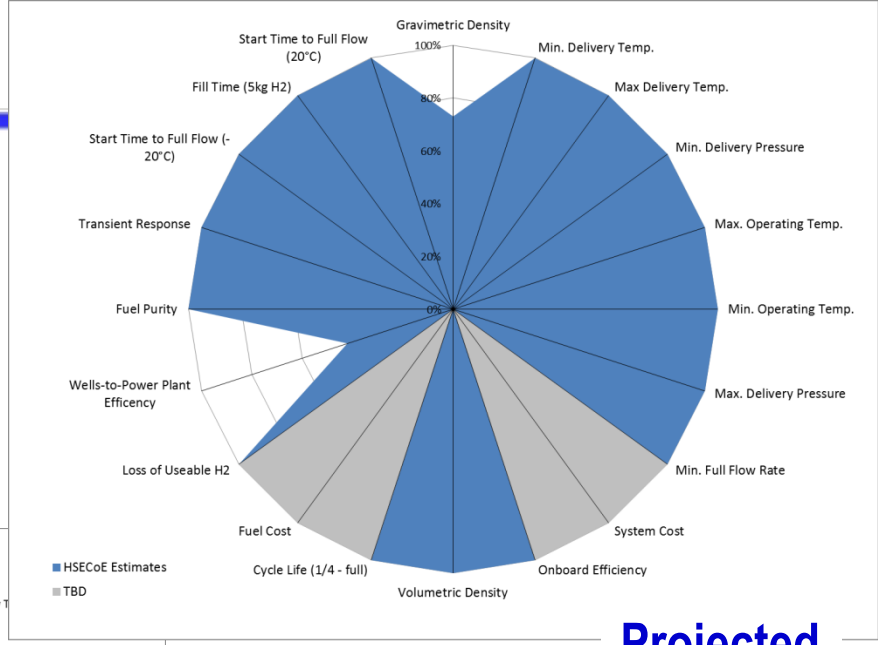
Notable Differences

- Recycle Loop replaced with Recuperator
- Eliminated one Heat Exchanger/Radiator
- Reduced H_2 Purification

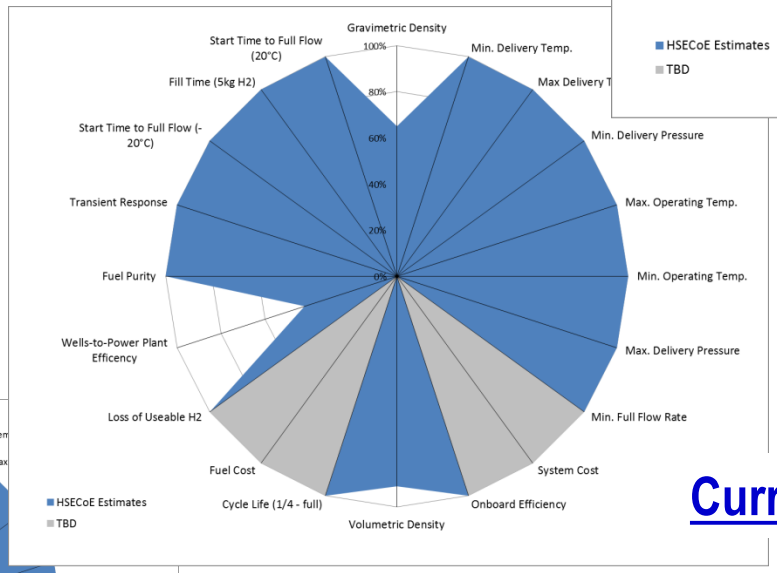
HSECoE

50 wt. % Alane Spider Charts

Endothermic Model



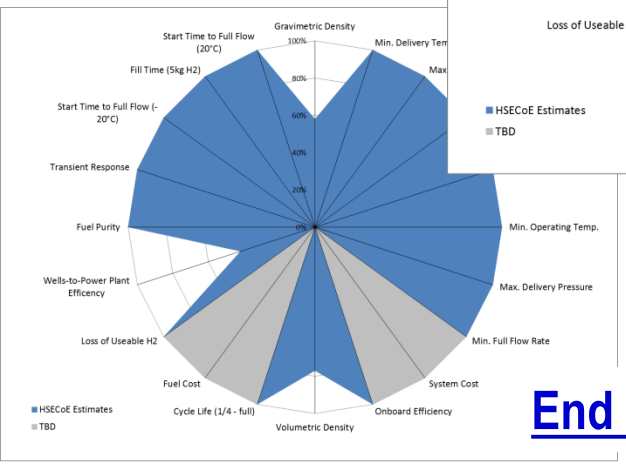
Projected



Current

HSECoE Estimates

TBD



End of Phase 1

FOCUS AREAS

System Mass

System Volume

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HSECoE

Projected Improvements for Alane Slurry System

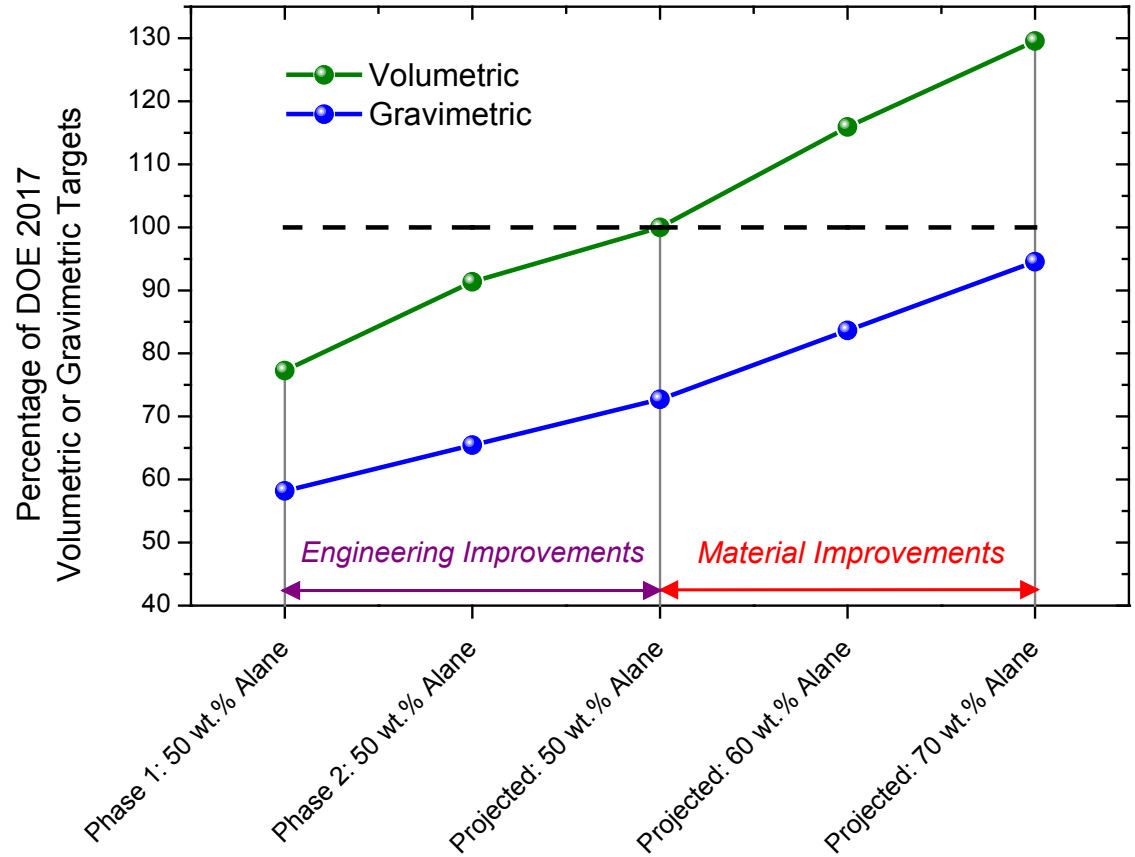
Engineering Improvements

Phase 1 to Phase 2 (Current)

- Phase 2 Component Validation Results
- Reduction of H_2 Purification and Heat Exchangers
- Higher fidelity System Models and System Designs

Phase 2 (Current) to Projected

- Similar approaches as those taken for the AB system



Material Improvements

Alane slurry loadings greater than 70 wt.% (~ 8.4 wt.% H_2) are expected to meet the DOE 2017 mass and volumetric targets

System Architect Accomplishments/Highlights

- Chemical Hydrogen Storage **System Architect** & **Fluid-Phase System Designer**
  - ✓ Developed and assessed endothermic and exothermic system designs and models
  - ✓ Identified material operating limitations for the on-board production of hydrogen
  - ✓ Performed component validation tests (e.g., GLS, VDT, H_2 purification, reactors, etc.,)
  - ✓ Refined system level models and designs from Phase 2 component validation efforts
  - ✓ Identified system engineering improvements for system mass, system volume, system cost, component manufacturability, system complexity, and system performance

LANL Technical Section

1. Reactors and Reaction Characteristics
   - *LANL Objectives and Relevance*
   - *Accomplishments*
2. Hydrogen Purification
   - *LANL Objectives and Relevance*
   - *Accomplishments*

Objectives: Reactor Design and Reaction Characteristics

1. *To demonstrate the reactive transport of slurry-phase chemical hydrogen storage materials*
2. *To collect the highest quality kinetics data for model validation*

- Data Collected
  - Temperature
  - Gas phase analyses (impurities and hydrogen)
  - Reactor performance (conversions, selectivities,etc.,)
  - Material performance and limitations

→ **Model Validity**

- Materials Tested
  - Slurry AB (exothermic)
  - Slurry Alane (endothermic)
  - Liquid MPAB (exothermic)

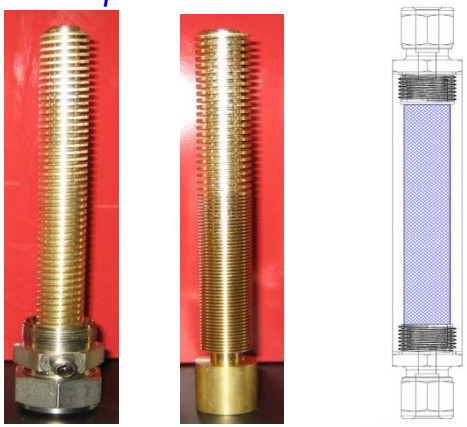
→ **Model Breadth**

- Reactors Tested
  - Auger (slurry alane and slurry AB)
  - Helical reactors (MPAB)
  - Packed-bed (MPAB)

→ **System Performance**

Approaches

Liquid Phase Reactors



B O PB

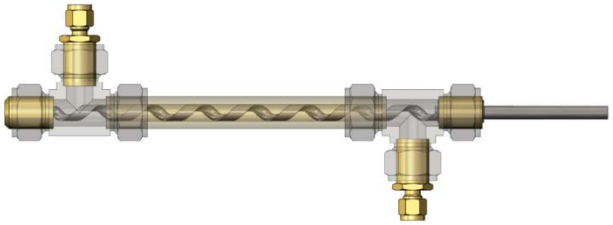
Technical Limitation: Reactant slugging

Our Method: Design reactors that prevent or minimize reactant slugging

2013 Goals: Design, build and test helical and packed-bed reactors with liquid-phase MPAB coupled with gas-phase analyses

Prevent reactant slugging

Slurry Phase Reactor



Technical Limitation: Reactor fouling and reactant slugging

Our Method: Design reactors that prevent or minimize reactant slugging and mitigate reactor fouling

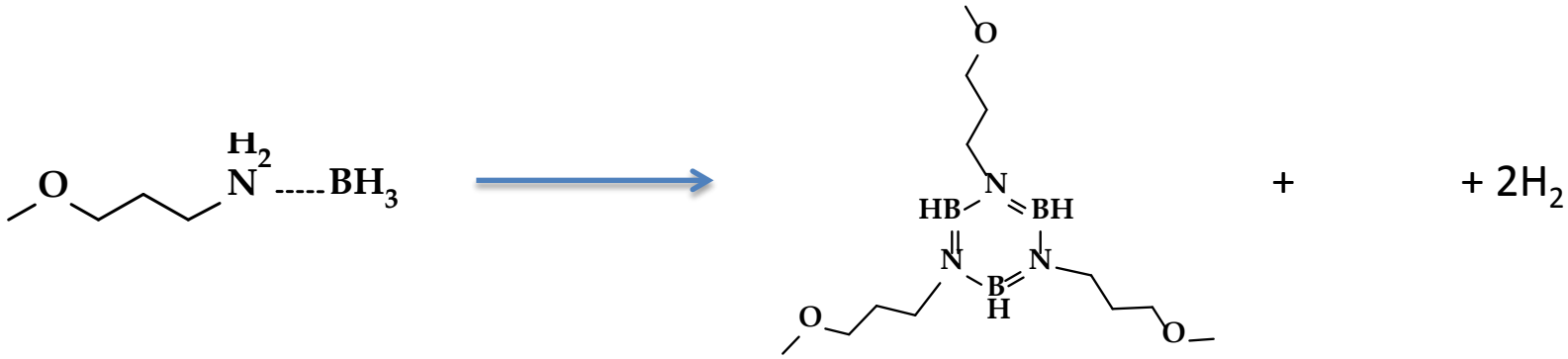
2013 Goals: Design, build and test auger reactor for slurry-phase alane and slurry phase AB coupled with gas-phase analyses

Prevent reactant slugging & mitigate reactor fouling

Three different reactors were examined with liquid phase MPAB

In-house built auger reactor was examined with slurry phase ALANE and AB

Methoxypropyl Amine Borane (MPAB) (exothermic liquid)



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MPAB Reactor Tests

Liquid Exothermic Material

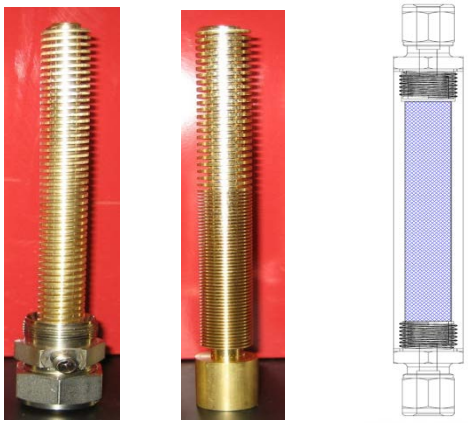
Prepared by Ben L. Davis and Brian D. Rekken

Composition:

- Neat methoxy propyl amine borane: 3.9 wt. % H_2

Reactors Tested:

- Helical reactors
- packed-bed reactor



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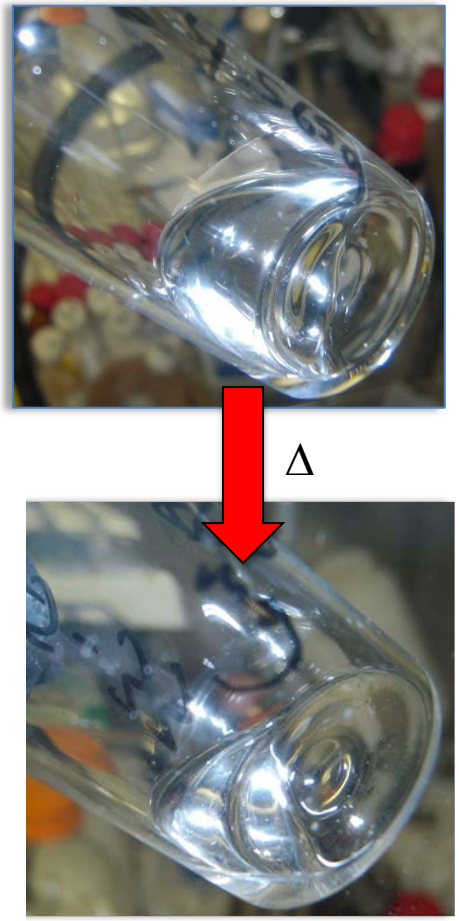


Operating Conditions

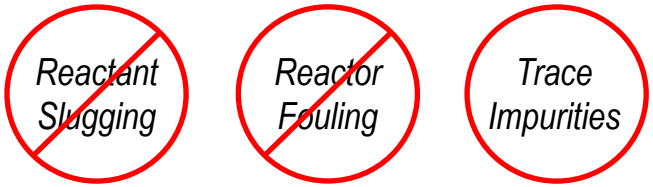
- Downward flow
- Liquid flow rates = 0.5-1.5 mL/min
- Reactor Set-point Temperatures = 50-225 °C

MPAB Accomplishments

Liquid Exothermic Material

Key Results

1. Successful demonstration of MPAB dehydrogenation as a function of reactor type, space-times and temperatures

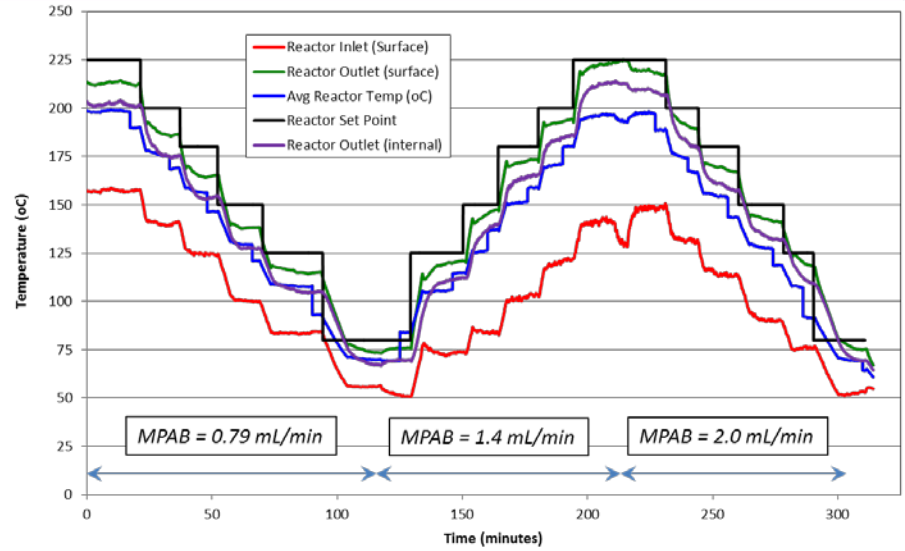


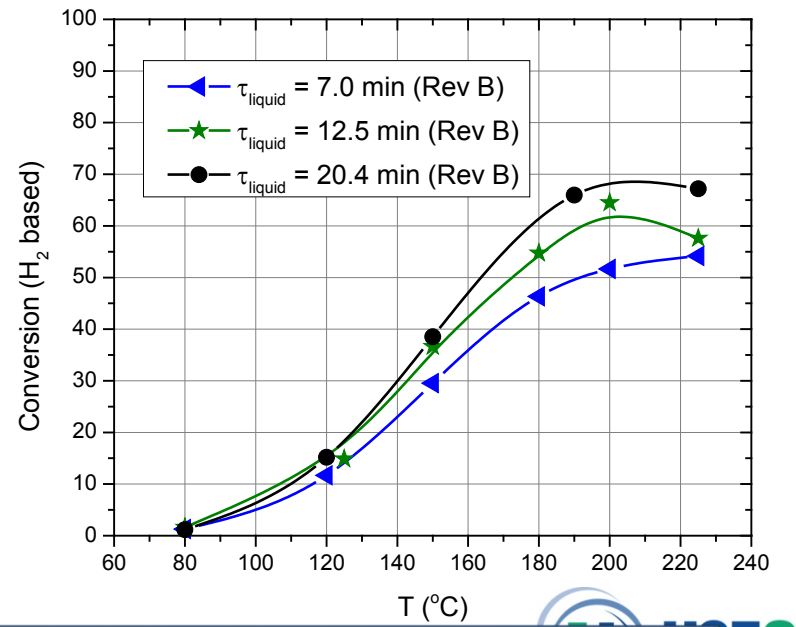
2. Full conversion of MPAB was not observed over the temperatures, space-times, or reactors investigated

$$X_{MPAB}\Big|_{max}^{\mathrm{Rev}\ B} \approx 66\%$$

3. Borazine, and ammonia were below detectable limits (100 ppm) and only trace amounts of diborane (~200 ppm)

4. MPAB conversion was limited to less than 66% because of the increased partial pressure of MPAB for temperatures greater than 180 °C





Research findings provided to materials researcher Ben L. Davis

Slurry ALANE
(endothermic slurry)

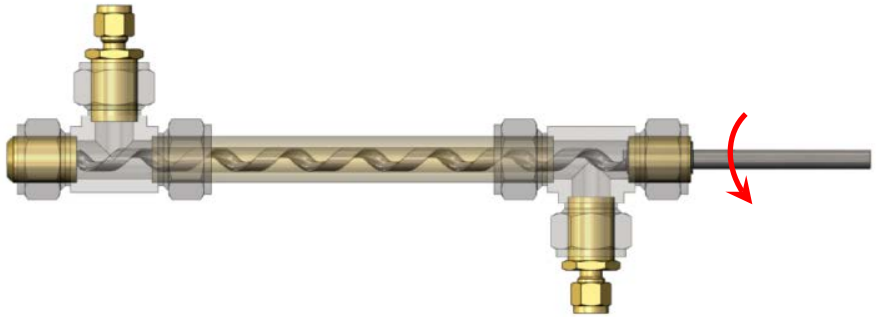
$$\left(AlH_3\right)_{slurry} \xrightarrow{\Delta} \left(Al\right)_{slurry} + 1.5H_2$$

$$\Delta H_{rxn} \approx +11 \frac{kJ}{mol\ AlH_3}$$

$$wt.\%\ H_2 \approx 10\ wt.\%$$

Slurry ALANE Accomplishments

Auger Slurry Reactor

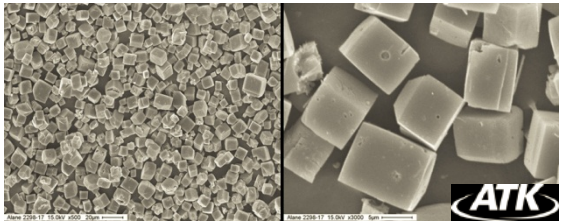


Reactor	Volume	Heated Reactor Length
	(mL)	(cm)
Auger-1	7.4	19.1

Alane Slurry Composition:

- 20 wt. % Alane (ATK): 2.00 wt. % H_2
- As-received ATK Alane
- AR 200 Silicon Oil (200 cP)
- Triton™ X-15 (0.025 g X-15/g Alane)

Note: alane slurry composition was "uncatalyzed"



Prepared by T.A. Semelsberger

Typical Operating Conditions

- Auger Speed: 40 rpm
- Horizontal Flow
- Reactor Temp: 125-275 °C
- Feed Flow Rates: 0.55-1.09 mL/min

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Slurry ALANE Accomplishments

Key Results

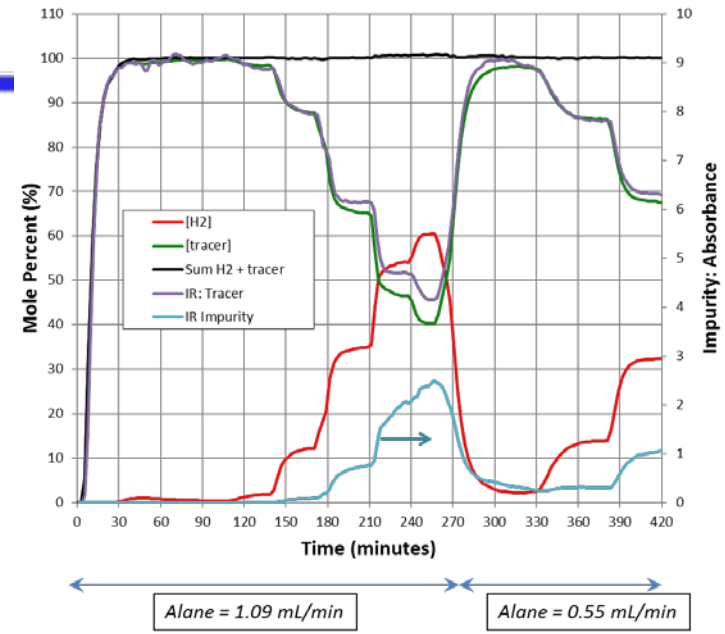
1. Successful demonstration of slurry ALANE dehydrogenation as a function of space-time and temperature with auger reactor

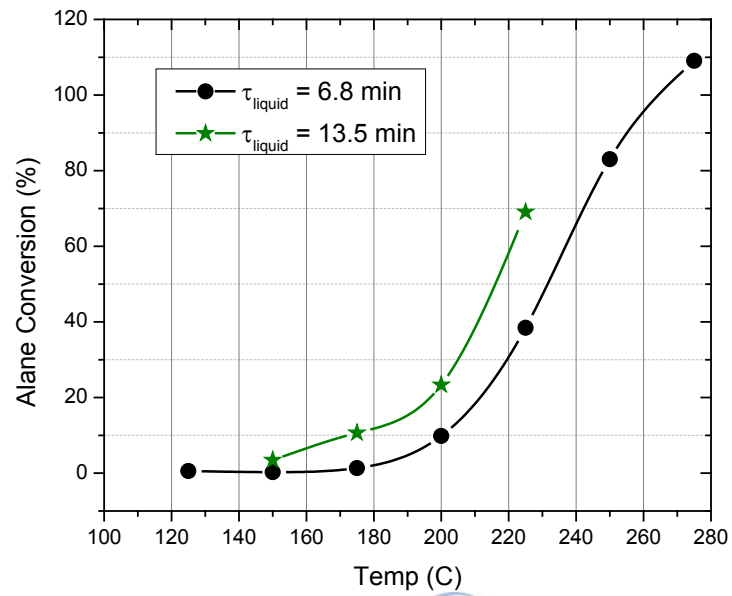
2. Full conversion of ALANE can be achieved

$$X_{Alane}\Big|_{max}^{auger} \approx 100\% @\ T_{avg} \approx 270^{\circ}C$$

3. Ti doped ALANE and/or ALANE activation will be required to lower the dehydrogenation temperature

4. Decomposition of silicon oil was observed for reactor set point temperatures greater than 225 °C and is the determinant factor for observed alane conversions greater than 1

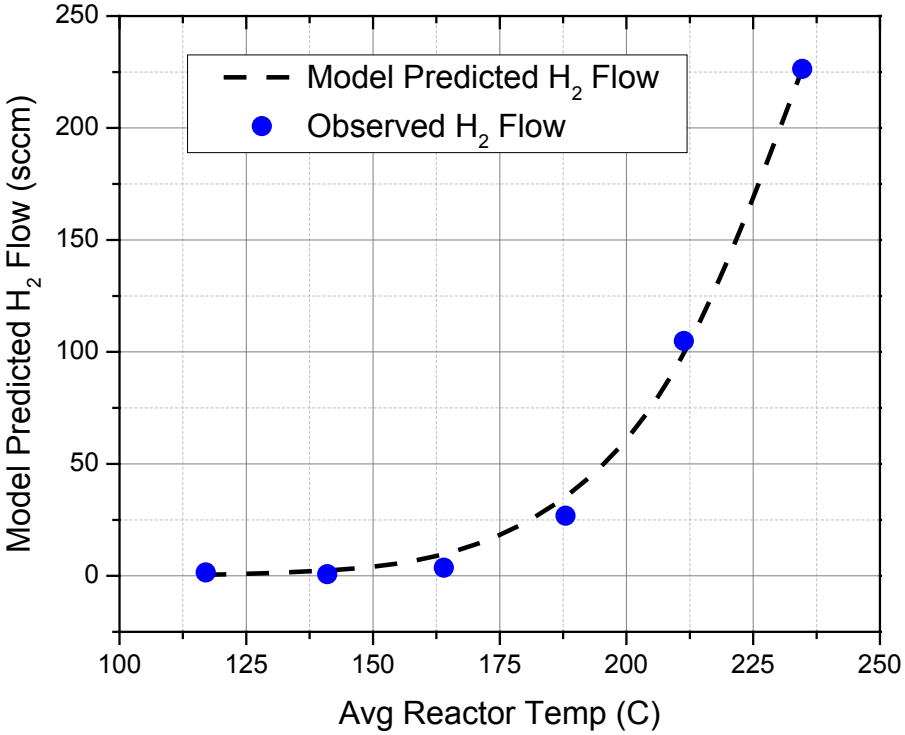


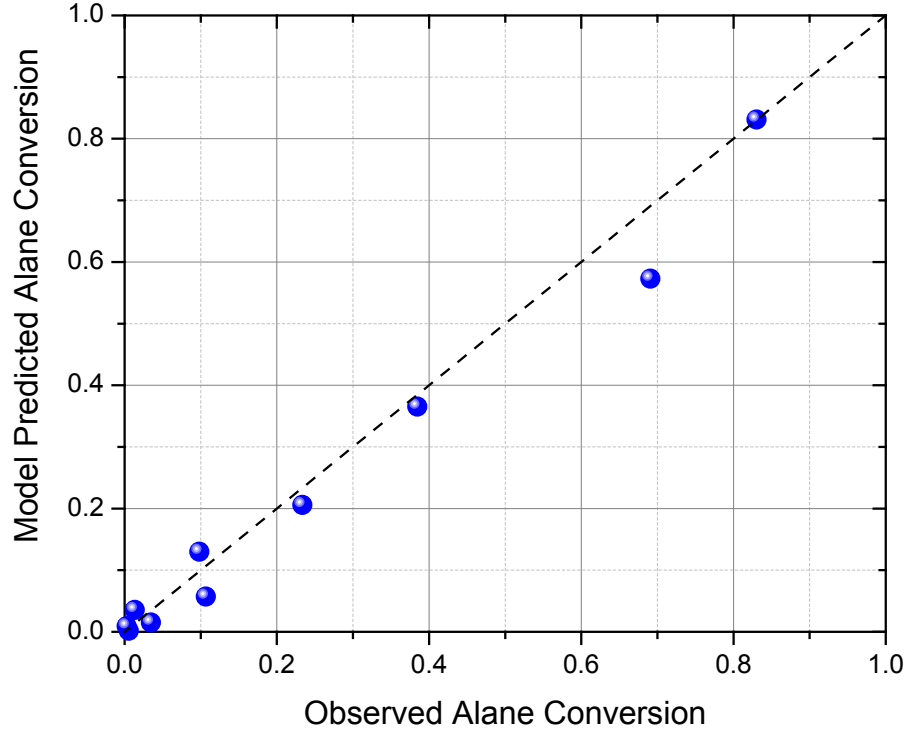


Slurry ALANE Accomplishments

$$-r_{Alane}\Big|_{apparent} = k(T)C_{alane}^{0.5} \qquad k(T) = Ae^{\left(\frac{-E_a}{RT}\right)}, \quad A = 3.7x10^6, \quad E_a = 90.75\frac{kJ}{mol}$$

Note: rate expression regressed with apparent kinetics for as-received alane collected with auger reactor





√ Model predictions agree with experiment

Rate expression provided to System Modeler, Kriston Brooks

Slurry AB
(exothermic slurry)

$$NH_3BH_3 \xrightarrow{\Delta} B_xN_yH_z + 2.35H_2 + NH3 + B_3N_3H_6 + B_2H_6$$

$$\Delta H_{rxn} \approx -49 \frac{kJ}{mol\ AB} \qquad wt.\%\ H_2\big|_{AB} \approx 15.2\ wt.\%$$

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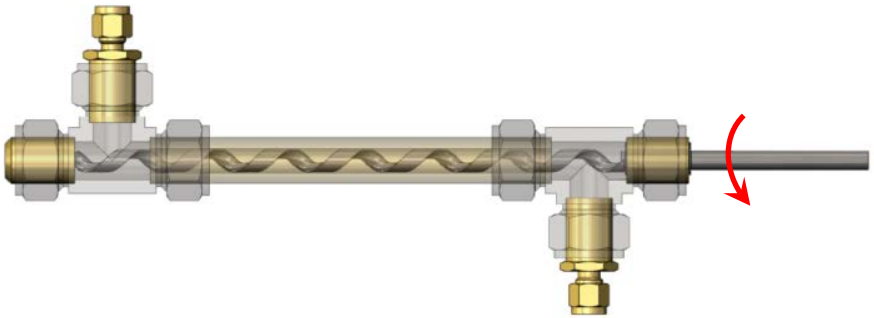
Slurry AB Accomplishments

Auger Slurry Reactor



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Typical Operating Conditions

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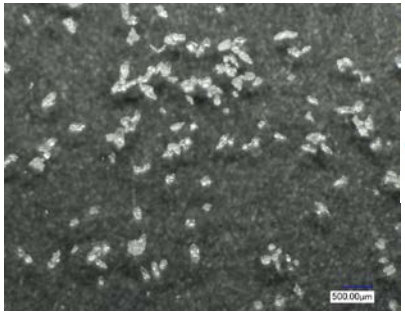
- Feed Flow Rates: 0.55-1.09 mL/min

AB Slurry Composition:

- 20 wt. % AB: 3.05 wt. % H_2
- AR 20 Silicon Oil (20 cP)
- Triton™ X-15 (0.025 g X-15/g AB)



WEYLCHEM

Stirred	Flocculated

Prepared by
Ewa Rönnebro

Pacific Northwest NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY EST. 1943

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Slurry AB Accomplishments

Key Results

1. Successful demonstration of slurry AB dehydrogenation as a function of space-time and temperature with auger reactor

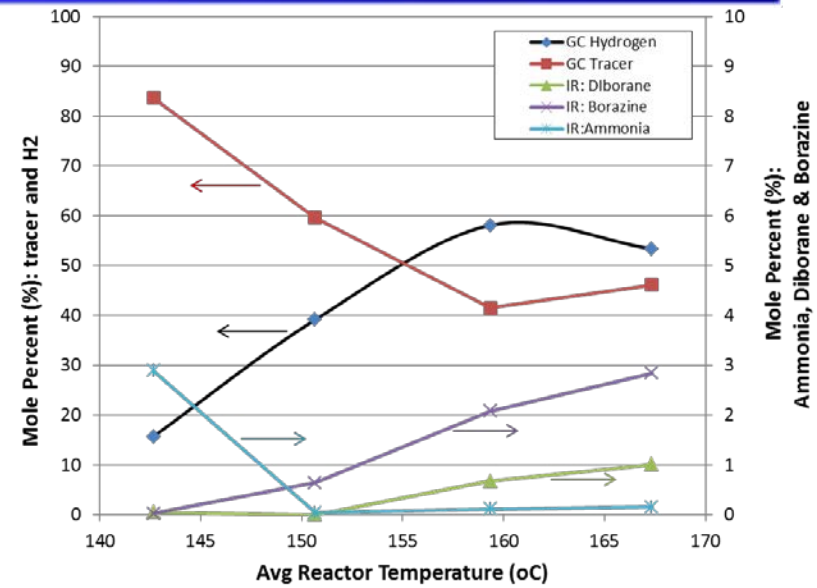
2. Full conversion of MPAB can be achieved but was not observed over the temperatures and space-times investigated

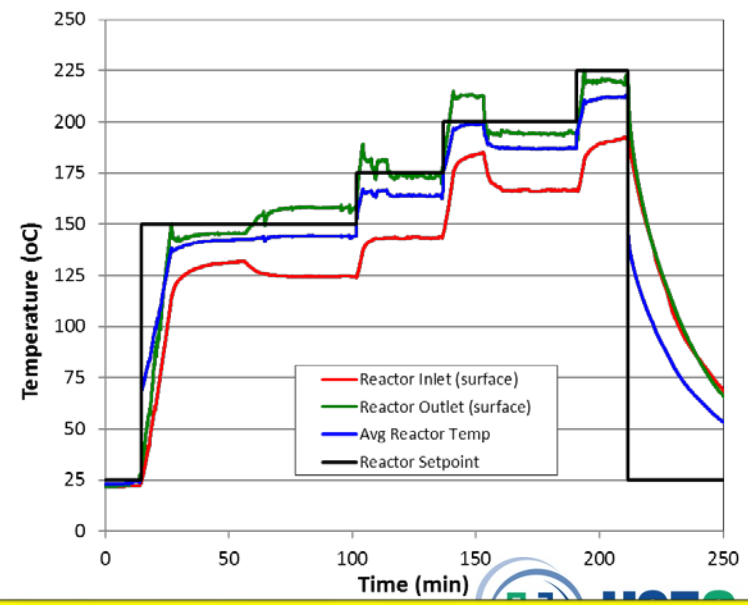
$$X_{AB}\Big|_{max}^{auger} \approx 86\% @\ T_{avg} \approx 212^{\circ}C$$

3. Maximum impurities observed during operation

$$\left[\left(n/n\%\right)_{NH_3}\right]_{\max}^{T=145} \approx 3.0\% \qquad \left[\left(n/n\%\right)_{diborane}\right]_{\max}^{T=168} \approx 1.0\%$$

$$\left[\left(n/n\%\right)_{borazine}\right]_{\max}^{T=168} \approx 2.8\%$$





Auger reactor performed equally well for both *ENDOTHERMIC* and *EXOTHERMIC* media types

LANL Technical Section

2. Hydrogen Purification
   - *LANL Objectives and Relevance*
   - *Accomplishments*

Borazine Adsorption Approaches

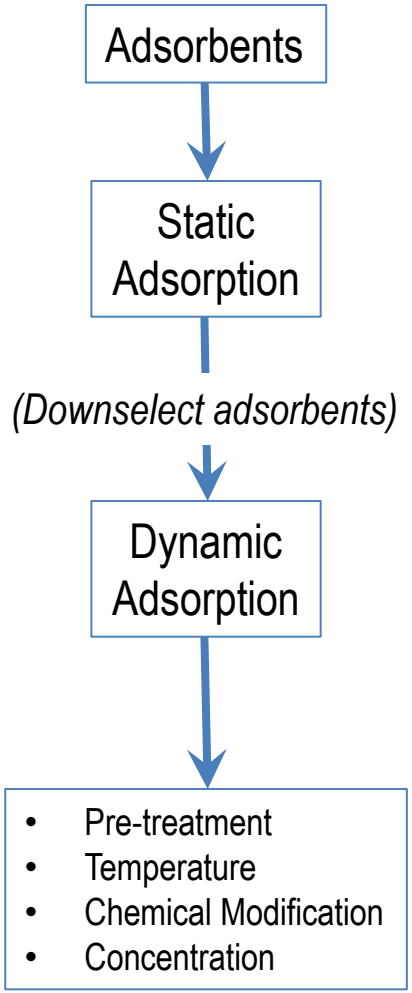
Technical Limitation: Borazine and ammonia are known fuel cell impurities generated from ammonia borane

Our Methods:

1. Develop and screen for potential borazine adsorbents
2. Implement ammonia adsorbent (UTRC) with down-selected borazine adsorbent (LANL) to demonstrate hydrogen purification

2013 Goals:

1. Down select borazine adsorbent with the highest borazine adsorption capacity
2. Demonstrate ammonia and borazine that is co-fed can be scrubbed to produce fuel-cell grade hydrogen



> 15 different adsorbents were screened for borazine adsorption capacity

Borazine Adsorption Accomplishments

Key Results

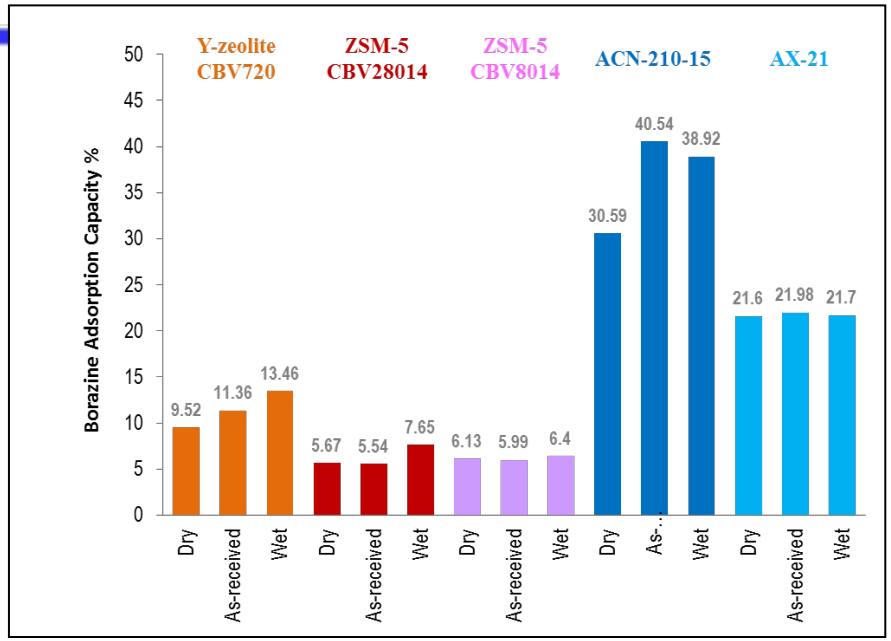
1. ACN-210-15 demonstrated the highest borazine adsorption capacity around 40% (P_{amb}) & 80% (P = 5 bar)

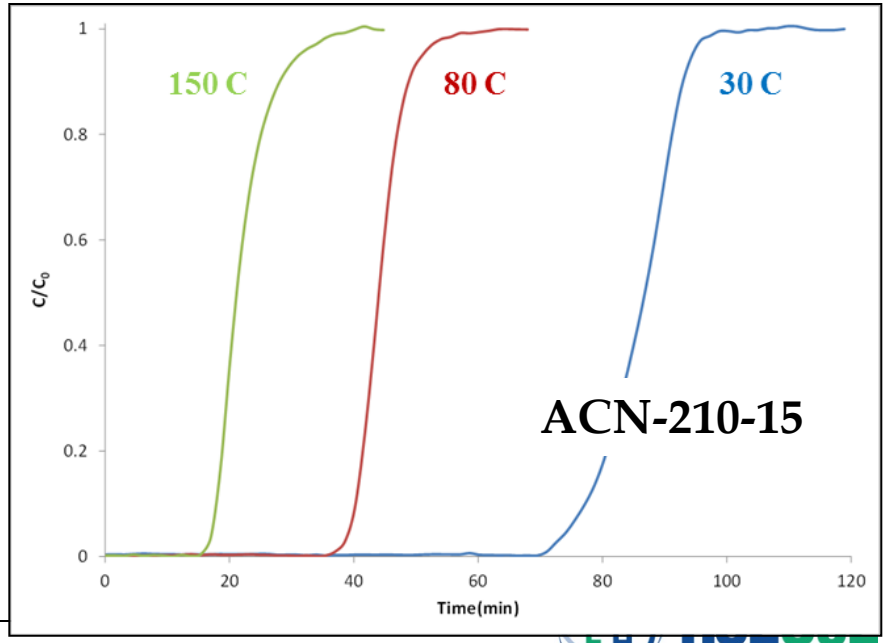
   ACN-210-15> AX-21> Y-zeolite > ZSM-5 > Oxides

   Note: Chemically modified substrates did not show marked improvements over the as-received analogs

2. ACN-210-15 is an off-the-shelf carbon adsorbent requiring no special pretreatments or handling
3. ACN-210-15 is a woven felt that is ideally suited for vibration prone environments because ACN-210-15 is not friable
4. Adsorption capacity decreases with increasing temperature

ACN-210-15 Down Selected



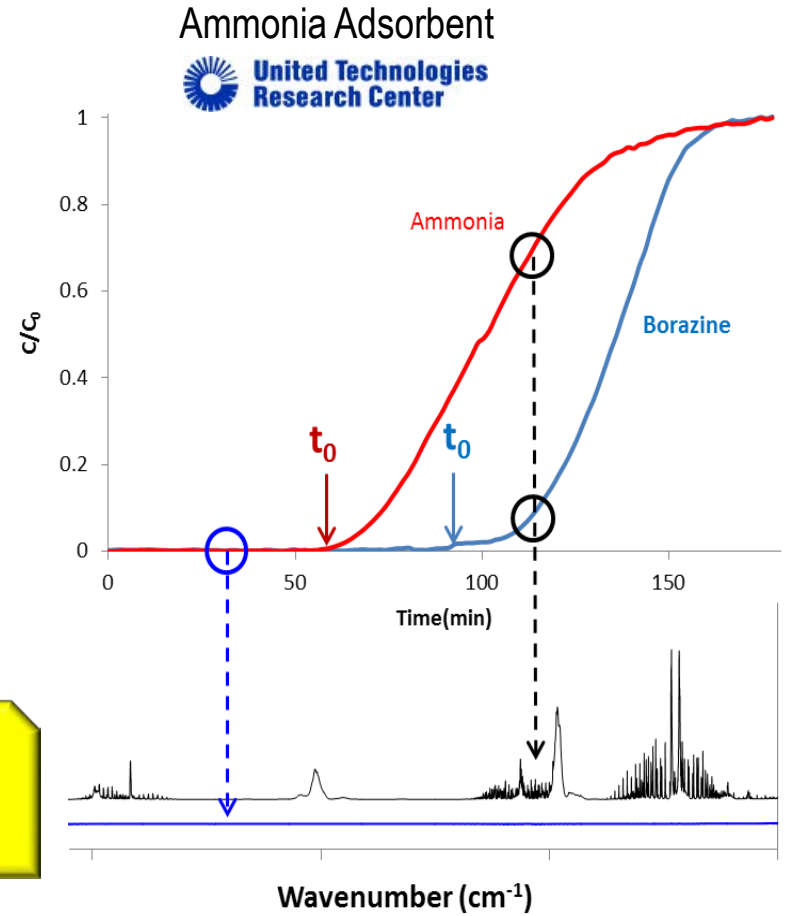


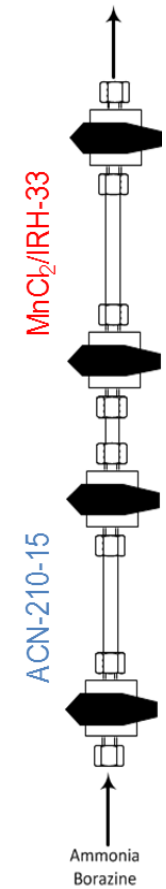
Ammonia and Borazine Adsorption Accomplishments

Key Results

1. Borazine has a higher chemical affinity toward $MnCl_2$ than ammonia has toward ACN-210-15
   - Ammonia adsorption capacity in ACN-210-15 ~ 1%
   - Borazine adsorption capacity in $MnCl_2$ ~ 6%
2. Adsorbent bed configuration is important
   - ➢ *Borazine should be scrubbed prior to Ammonia*

Ammonia and borazine can be scrubbed to produce fuel-cell grade hydrogen





We have identified potential scrubbing technologies that can reduce the current requirement of 6.8 kg of ACN-210-15

Summary: 2013 Accomplishments

- Successfully demonstrated flow reactor tests with quantification on slurry *ALANE*, slurry *AMMONIA BORANE*, and liquid *MPAB*
- Full conversion of "uncatalyzed" *ALANE* can be achieved for temperatures greater than 270 C
- Improvements in *ALANE* dehydrogenation kinetics were observed with the use of dopants and solvents *(reviewer only slides)*
- No impurities were detected during *ALANE* dehydrogenation
- Trace amounts of diborane were detected during *MPAB* dehydrogenation
- *AMMONIA BORANE* produced borazine, diborane, and ammonia impurities
- Reactant slugging and reactor fouling were mitigated through our in-house designed and built reactors
- In-house built auger reactor performed equally well for both slurry *ALANE* and slurry *AMMONIA BORANE* compositions
- ACN-210-15 demonstrated the highest borazine adsorption capacity
- Demonstrated that ammonia and borazine can be scrubbed to produce fuel-cell grade hydrogen

LANL Future Work

1. Slurry AB Compositions (exothermic)
   - *Perform kinetics/reactor tests with increased AB loadings (30-50 wt. %); develop rate expression*
2. Slurry Alane Compositions (endothermic)
   - *Perform kinetics/reactor tests with increased alane loadings (40- 60 wt.%); develop rate expression*
   - *Extend alane kinetics/reactor tests to include different solvents (e.g., DEGB) and dopants (e.g., Ti)*
3. Liquid MPAB (exothermic)
   - *Redesign reactor to address material limitation*
4. Borazine Scrubbing
   - *Examine non-adsorbent based borazine scrubbing technologies*

Collaborations

External Collaborators	Effort	Contact
H_2 Codes and Standards	General Guidance	C. Padro (LANL)
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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Acknowledgements

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Ned Stetson and Jessie Adams

Backup Slides

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HSECoE Partners

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The Chemical Company

Supporting Information

SMART Milestones

Chemical Hydrogen Storage Team				
Component	Lead	S*M*A*R*T Milestone	Status 20 Mar 2013	Projected Outcome
Materials Development	LANL	Report on ability to develop a 40wt% liquid AB material (6.4wt%H2) having viscosity less than 1500cP pre- and post-dehydrogenation and kinetics comparable to the neat.	Developed a 3.9 wt.% H2 liquid phase chemical hydrogen storage media that is liquid both pre- and post-reaction with kinetics similar to that of solid AB, preliminary impurities profile looks promising because of the significantly reduced or eliminated impurities production, viscosities all well below 1500cP	Investigations will continue into new solvent chemistries which are anticipated to meet the metric while minimizing fuel-cell impurities
Materials Development	PNNL	Report on ability to develop a 40wt. % slurry AB material having viscosity less than 1500cP pre- and post-dehydrogenation and kinetics comparable to the neat.	45wt% AB achieved before reaction 617cP, Yield stress 48 Pa after dehydrogenation 442cP, yield stress 3.7Pa	**Met Target**
Reactor	LANL	Report on ability to develop a flow through reactor capable of discharging 0.8 g/s H2 from a 40 wt.% AB fluid-phase composition having a mass of no more than 2 kg and a volume of no more than 1 liter.	Reactor performance and Kinetics collected for • Liquid exothermic material (3.9 wt.% H2-MPAB) • Slurry exothermic material (20 wt.% AB slurry) • Slurry endothermic material (20 wt.% Alane) *Data will be provided to Kriston to incorporate into system-level model*	Reactor performance tests kinetics will be performed on • 35-50 wt% AB slurries • 40-60 wt.% Alane slurries *Note: Alternative reactor designs and operation will be performed to maximize reactor efficiency* *Data will be provided to Kriston to incorporate into system-level model*
HX/Radiator	PNNL	Report on ability to develop/identify a radiator/HX capable of cooling the effluent from 525K to 360K having a mass less than 1.15 kg and a volume less than 10.9 liters	Radiator volume – 1.5L, mass 1.44kg, Validated models show a decrease in fins spacing will achieve the mass of 1.15kg mass and the required heat transfer meeting the metrics.	**Met Target**
GLS	UTRC	Report on ability to develop a GLS capable of handling 720 mL/min liquid phase and 600 L/min of H2 @ STP (40 wt% AB @ 2.35 Eq H2 and max H2 flow of 0.8 g/s H2) fluid having a viscosity less than 1500cp with resulting in a gas with less than 100ppm aerosol having a mass less than 5.4 kg and volume less than 19 liters.	Mass 5.8 kg (above 5.4 kg metric) Volume 2.7 L (far below 19 L metric).	**Exceeded volume target, but just over the mass target**. Demonstrate operation meeting metrics utilizing spent fuel simulant.
Borazine Scrubber	LANL	Report on ability to develop a borazine scrubber with a minimum replacement interval of 1800 miles of driving resulting in a minimum outlet borazine concentration of 0.1 ppm (inlet concentration = 4,000 ppm) having a maximum mass of 3.95 kg and maximum volume less of 3.6 liters.	An activated carbon borazine scrubber has been demonstrated yielding <0.1 ppm exit borazine concentration having: Mass = 6.8 kg (need significant reduction) Volume = 5.9 L (need reduction but not as critical as mass)	Alternative non-adsorbent based strategies are being explored to reduce the mass and volume of the scrubber.
Ammonia Scrubber	UTRC	Report on ability to develop an ammonia scrubber with a minimum replacement interval of 1800 miles of driving resulting in a minimum ammonia outlet concentration of 0.1 ppm (inlet concentration = 500 ppm)having a maximum mass of 1.2 kg and a maximum volume of 1.6 liters.	Mass 1.1 kg (surpass 1.2 kg metric) Volume 1.6 L (meets 1.6 L metric)	**Met Target**
BoP	PNNL	Report on ability to Identify BoP materials suitable for the Chemical Hydrogen system having a system mass no more than 41 kg and a system volume no more than 57 liters.	Mass = 60kg Volume = 61 L (really close to meeting volume target)	Critical reductions in mass: • borazine scrubber • pump mass • GLS mass • via parts consolidation/elimination/new technology *Note: in meeting the mass target, we will also meet the volume target*
System Design	PNNL	Report on ability to identify a system design having a mass less than 97 kg and a volume less than 118 liters meeting the all of the HSECoE drive cycles.	50%AB/Si oil : Media Mass = 97kg Media Volume = 86.5 L System Mass = 137 kg System Volume = 148 L	Alternate components and designs are being investigated but a higher density slurry (70w% AB or similar) will be required to meet the metric.
Efficiency Analysis	NREL	Calculate and model the well-to-powerplant (WTPP) efficiency for two chemical hydride (CH) storage system designs and compare results relative to the 60% technical target.	Alane 24.7% WTPP efficiency AB 16.5% WTPP efficiency	**Met Target**

Reactor Development and Performance

LANL TEAM

Troy A. Semelsberger, Jose .I. Tafoya, Ben. L. Davis, and Brian. D. Rekken

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T.A. Semelsberger

TTR Meeting
Detroit, Michigan March 20-21, 2013

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NREL National Renewable Energy Laboratory
Pacific Northwest NATIONAL LABORATORY
United Technologies Research Center
HSECoE

Materials Tested in Batch Reactor

- 20 wt.% ATK Alane DEGBE-uncatalyzed
- 20 wt.% ATK Alane Julabo H350-uncatalyzed
- 20 wt.% ATK Alane DEGBE/LiH/Ti-catalyzed
- 20 wt.% ATK Alane Julabo H350/LiH/Ti-catalyzed
- 20 wt.% Slurry AB/Silicon Oil
- 20 wt.% Liquid AB/Iolilyte

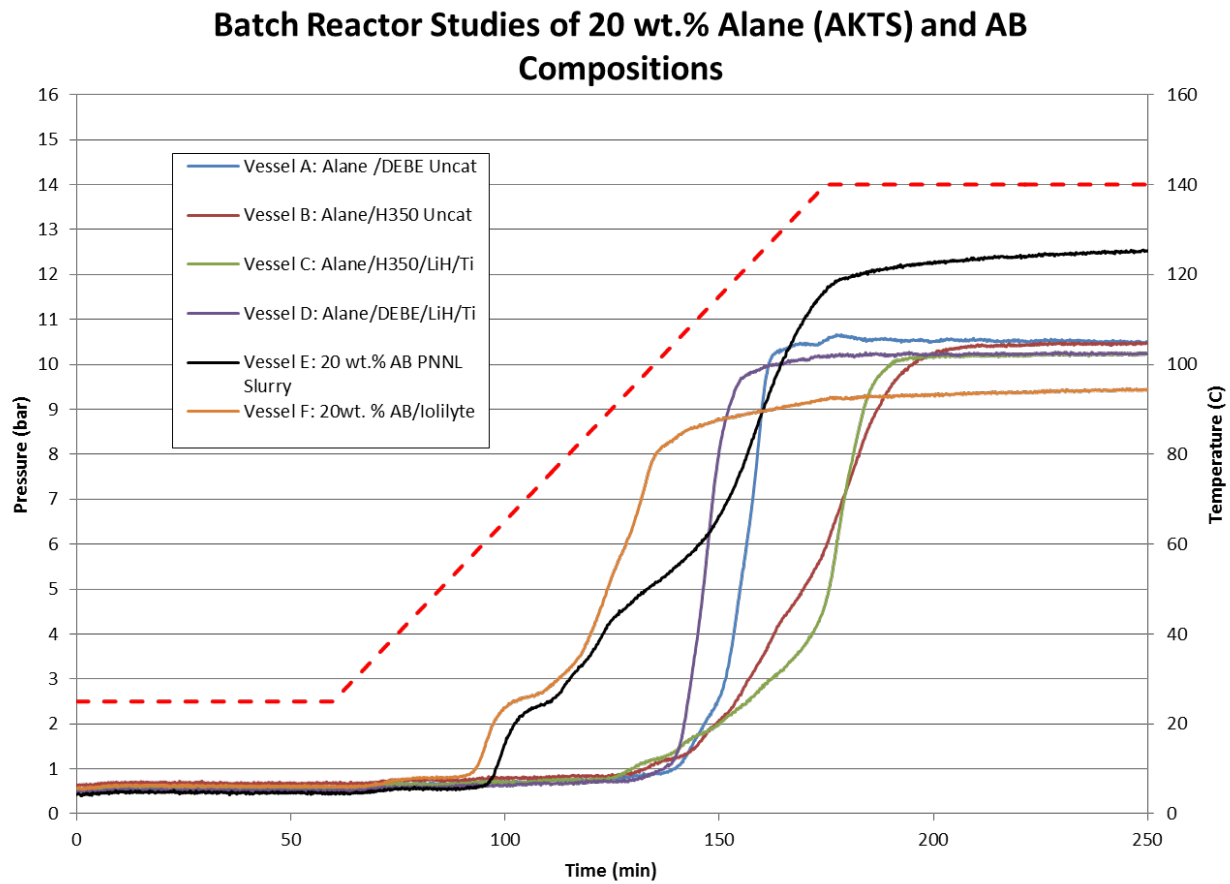
Temperature Profile:

Step 1: t_{iso} = 60 min @ T = 25 °C
Step 2: T_r = 1 °C/min with T_f = 140 °C
Step 3: t_{iso} = 2800 min @ T = 140 °C

Batch Reactor Screening of Ammonia Borane and Alane

Objectives:

1. Solvent Effects
2. Catalytic Effects



$$T_{onset}\Big|_{AB} < T_{onset}\Big|_{Alane}$$

Alane Batch Reactor Results

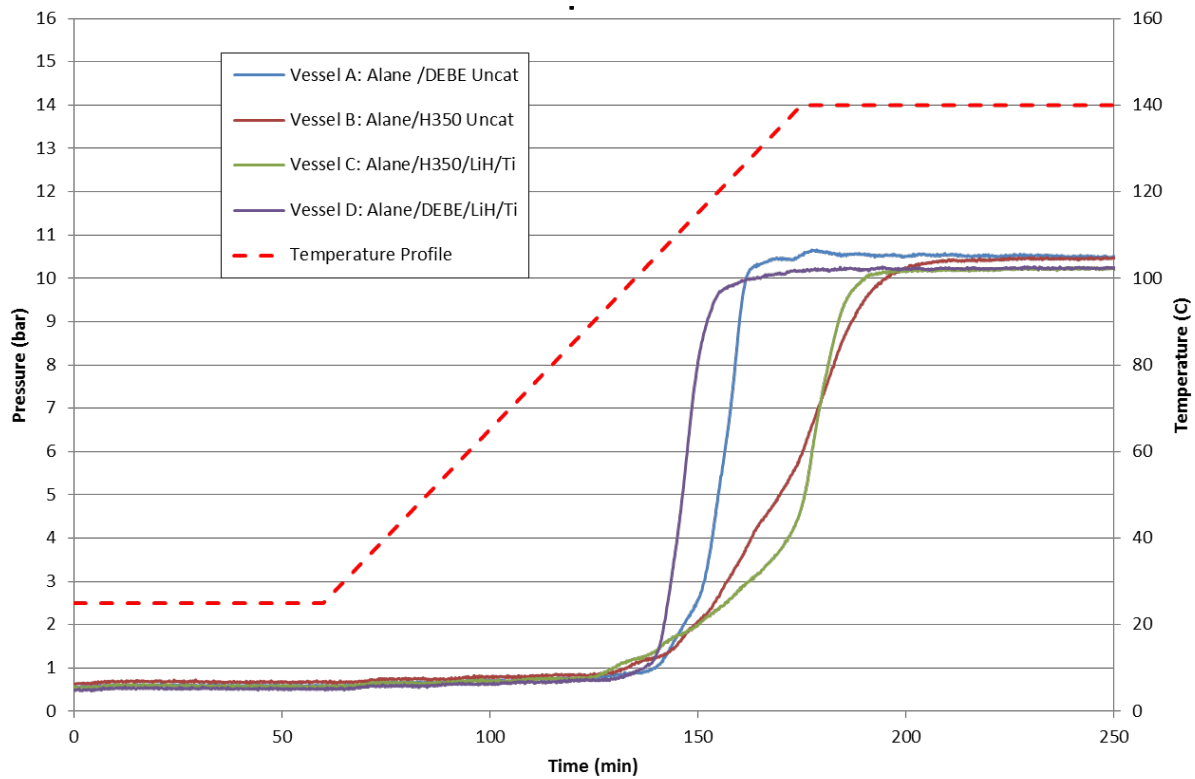
$$AlH_3 \xrightarrow{\Delta} Al + 1.5H_2$$

$$\Delta H_{rxn} \approx +11 \frac{kJ}{mol\ AlH_3}$$

$$wt.\%\ H_2 \approx 10\ wt.\%$$

- LiH and Ti improve kinetics of alane dehydrogenation in DEBE, but not in H350
- Solvent choice has a greater impact on alane dehydrogenation rate than LiH and Ti
- Dehydrogenation onset temperatures remain relatively unchanged wrt solvent or LiH/Ti

$$T_{onset} \approx 90^{\circ}C$$



AB Batch Reactor Results

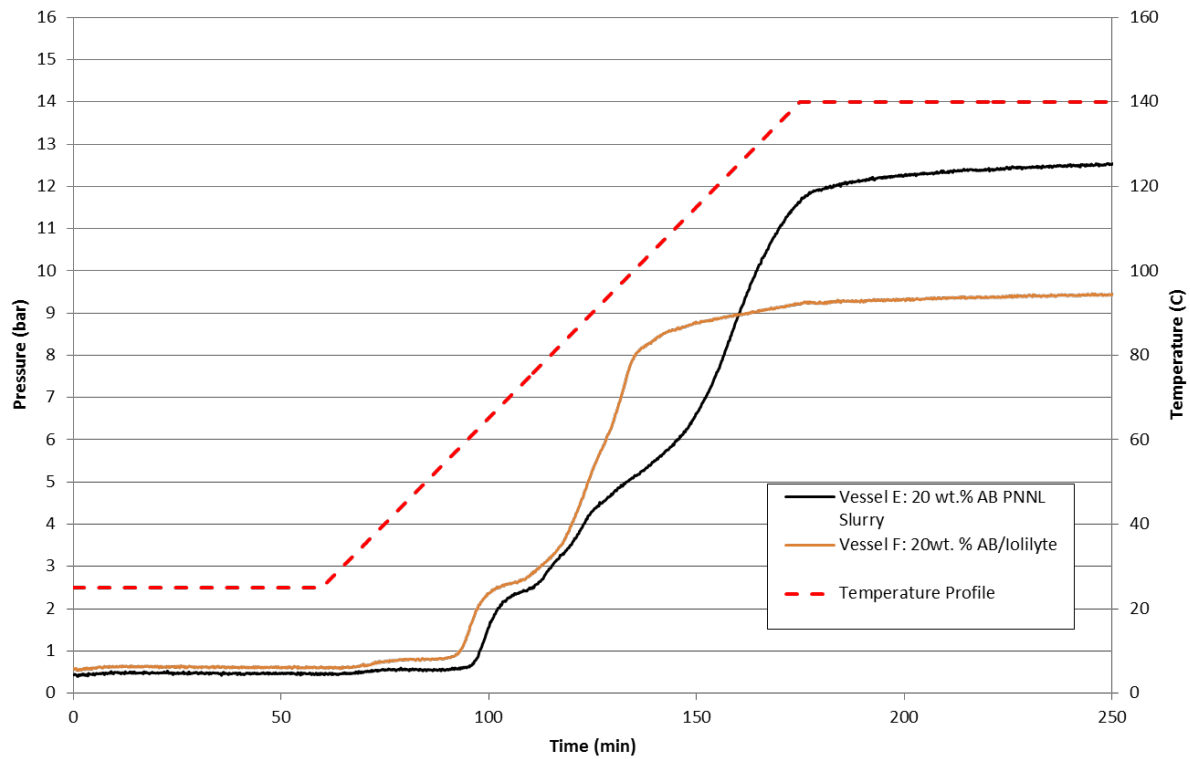
$$\Delta H_{rxn} \approx -49 \frac{kJ}{mol\ AB}$$

$$NH_3BH_3 \xrightarrow{\Delta} B_xN_yH_z + 2.35H_2 + NH3 + B_3N_3H_6 + B_2H_6$$

$$wt.\%\ H_2\big|_{AB} \approx 15.2\ wt.\%$$

- AB Slurry demonstrated a three step process consistent with prior observations
- AB/Iolilyte two-step process coupled with chemical incompatibility with iolilyte
- Dehydrogenation onset temperatures are approximately the same

$$T_{onset} \approx 55^{\circ}C$$



2. Flow Reactor Experiments

1. Batch Reactor Testing
   - AB Slurry
   - Alane Slurry
   - AB-IL

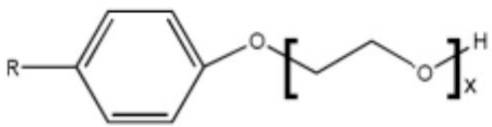
2. Flow Reactor Testing
   - MPAB (liquid exothermic material)
     - Helical Reactor (O)
     - Helical Reactor (A)
     - Packed-bed Reactor (PB)
   - AB Slurry (exothermic material)
     - Auger Reactor
   - Alane Slurry (endothermic material)
     - Auger Reactor

Alane Slurry Reactor Tests

Prepared by T.A. Semelsberger

Slurry Composition:

- 20 wt. % Alane (ATK): 2.00 wt. % H_2
- AR 200 Silicon Oil (200 cP)
- Triton™ X-15 (0.025 g X-15/g AB)



R = octyl (C8)
x = 1.5 (avg)

Triton™ X-15

Stirred Settled

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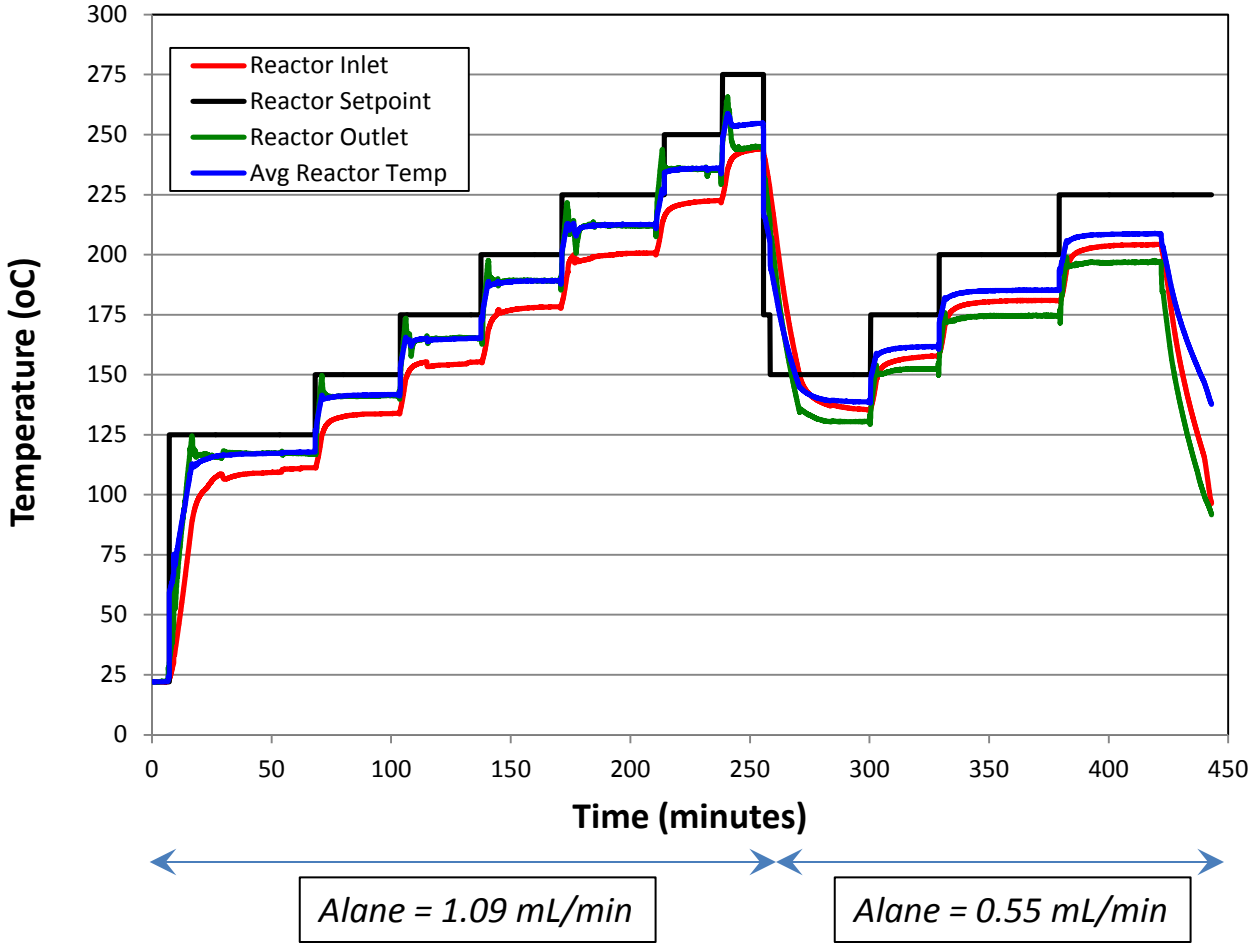
Alane Auger Reactor Results

20 wt.% Alane-07

- Auger Reactor (Volume = 7.4 mL)
- Reactor T_{stpt} = 125-275°C
- Feed Flow Rates:
  - 1.09 mL/min (6.8 min)
  - 0.55 mL/min (13.5 min)



- Alane flow-reactor experiment was well behaved and stable
- No observable endothermic temperature profiles

Alane Auger Reactor Results

20 wt.% Alane-07

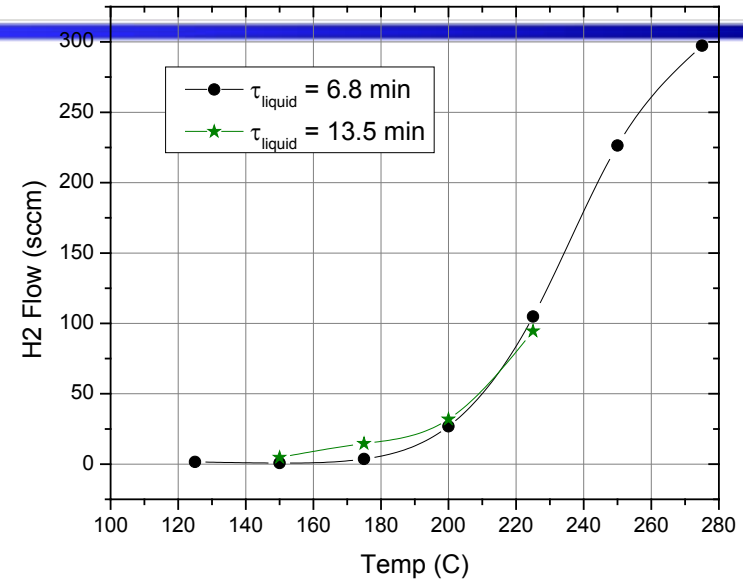
- Auger Reactor (Volume = 7.4 mL)
- Reactor T_{stpt} = 125-275°C
- Feed Flow Rates:
  - 1.09 mL/min (6.8 min)
  - 0.55 mL/min (13.5 min)

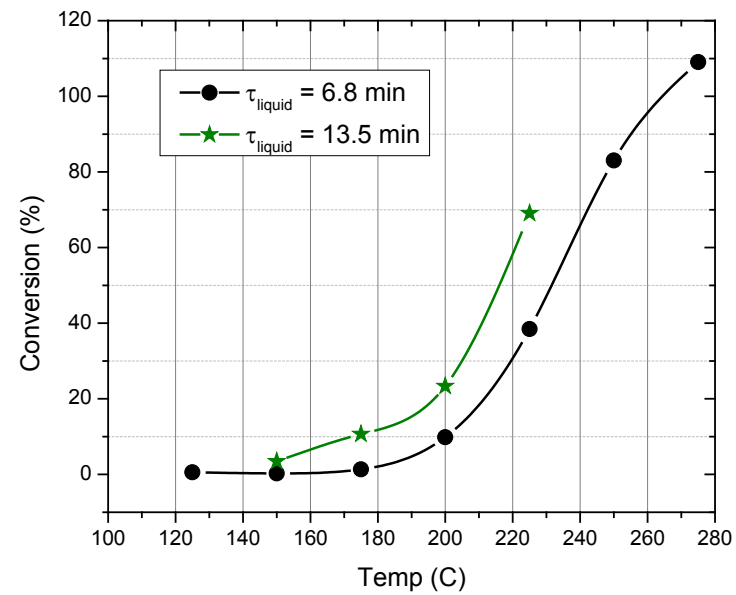
➢ Conversion and hydrogen flow rate increase with increasing temperature

$$X_{Alane}\Big|_{max} \approx 100\%$$

$$F_{H_2}\Big|_{max} \approx 300\ sccm$$

➢ Conversions greater than 100% were observed because of the decomposition of silicon oil and/or the chemical reaction of silicon oil with aluminum/alane…resulting in an increase in the observed hydrogen production





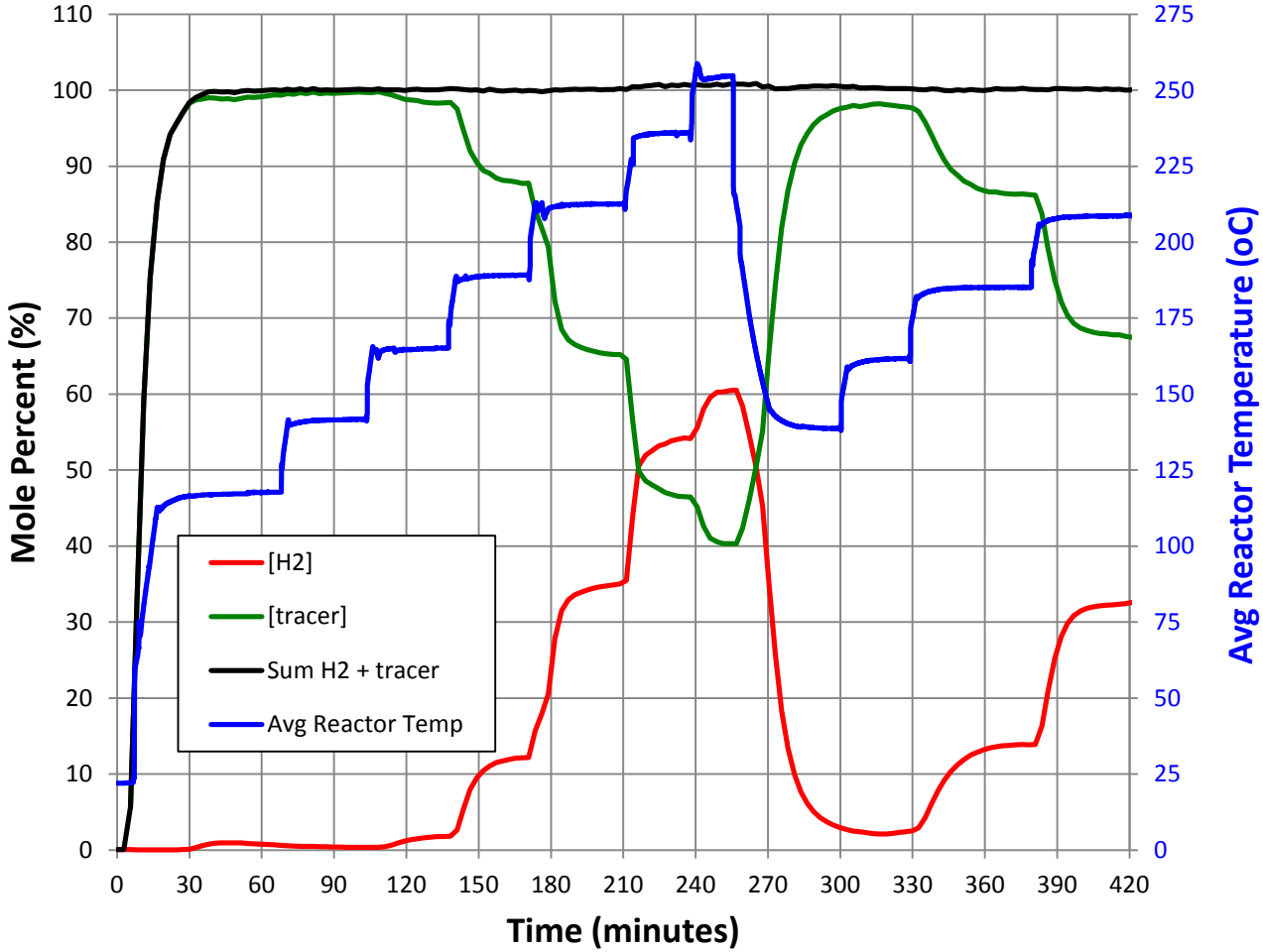
Alane Auger Reactor Results

20 wt.% Alane-07

- Auger Reactor (Volume = 7.4 mL)
- Reactor T_{stpt} = 125-275°C
- Feed Flow Rates:
  - 1.09 mL/min (6.8 min)
  - 0.55 mL/min (13.5 min)

- Hydrogen mole percentage tracks nicely with temperature
- The mole percentage totals sum to approximately 100%

$$180\ min \leq t \leq 330\ min$$



Alane = 1.09 mL/min

Alane = 0.55 mL/min

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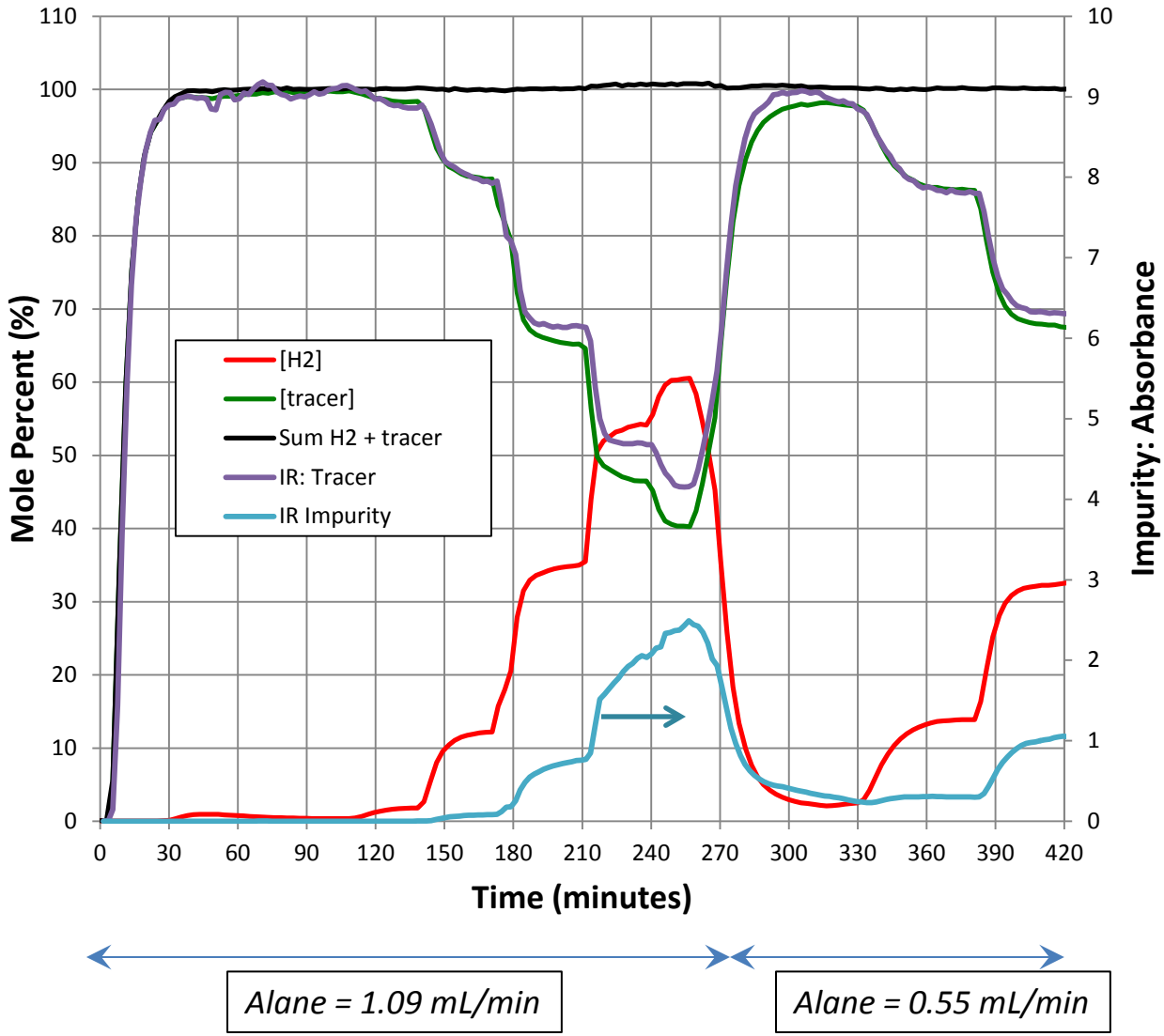
Alane Auger Reactor Results

20 wt.% Alane-07

- Auger Reactor (Volume = 7.4 mL)
- Reactor T_{stpt} = 125-275°C
- Feed Flow Rates:
  - 1.09 mL/min (6.8 min)
  - 0.55 mL/min (13.5 min)

- The only impurity observed was due to thermal decomposition of the silicon oil used as the carrier
- Maximum temperature of this alane composition is around T_{avg} ~210 °C



Summary: 20 wt.% Alane Slurry Reactor Results

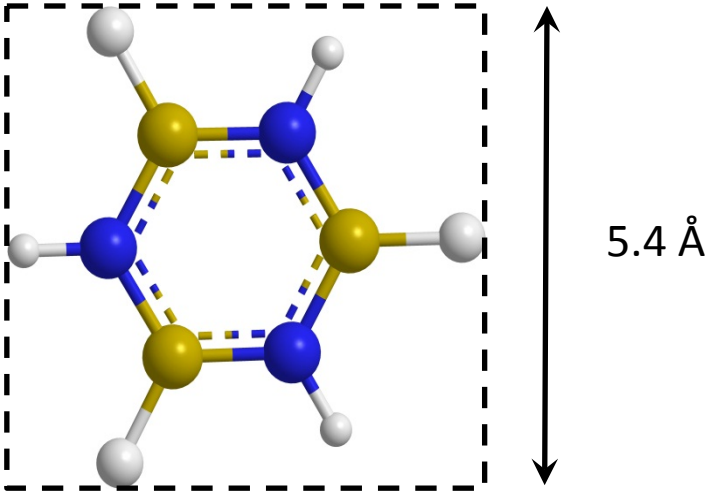
- Successful demonstration of a 20 wt. % alane slurry dehydrogenation as a function of temperature and space-time
- Full conversion of slurry alane was observed over the temperatures, and space-times investigated
  - Maximum conversion observed was X_{MPAB} ~100% @ τ_{liquid} = 6.8min and T = 260-275°C with in-house built auger reactor
- The only impurity observed during alane dehydrogenation was the degradation of the carrier (Reactor T_{stpt} = 225°C, T_{avg} = 210°C)
- The reaction was stable, clean and facile
- Improvements in the reaction kinetics can be accomplished by the use of dopants and alternative solvents

Slurry Endothermic Material

Borazine Adsorption

Borazine is a known fuel cell impurity that requires scrubbing

Relevance: To develop and demonstrate hydrogen purification technologies that produce fuel-cell grade hydrogen meeting DOE purity targets



Borazine

Component	Partner	S*M*A*R*T Milestone
Borazine Scrubber	LANL	Report on ability to develop a borazine scrubber with a minimum replacment interval of 1800 miles of driving resulting in a minimum outlet borazine concentration of 0.1 ppm (inlet concentration = 4,000 ppm) having a maximum mass of 3.95 kg and maximum volume less of 3.6 liters.

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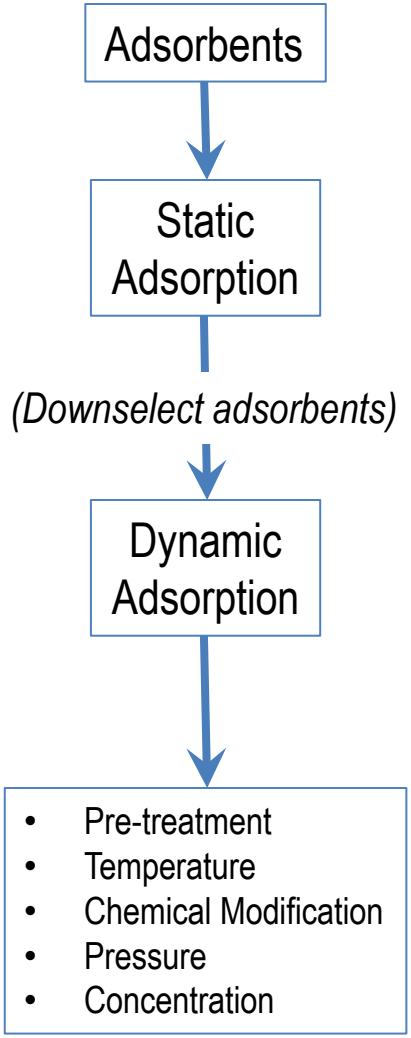
Approach

Screen adsorbents for borazine adsorption capacities at RT under static adsorption conditions

- ✓ Adsorbents dried under Ar flow at 200 C for 2 hr
- ✓ Adsorbents kept under sealed borazine gas environment for several days
- ✓ Mass gain is measured to estimate the borazine adsorption capacity under the static adsorption

Downselect adsorbents to determine the dynamic adsorption capacities of borazine

Dynamic adsorption mimics closely the situation where impurity gases (produced by the decomposition of AB-based H_2 storage system) flow through the adsorbent (s)



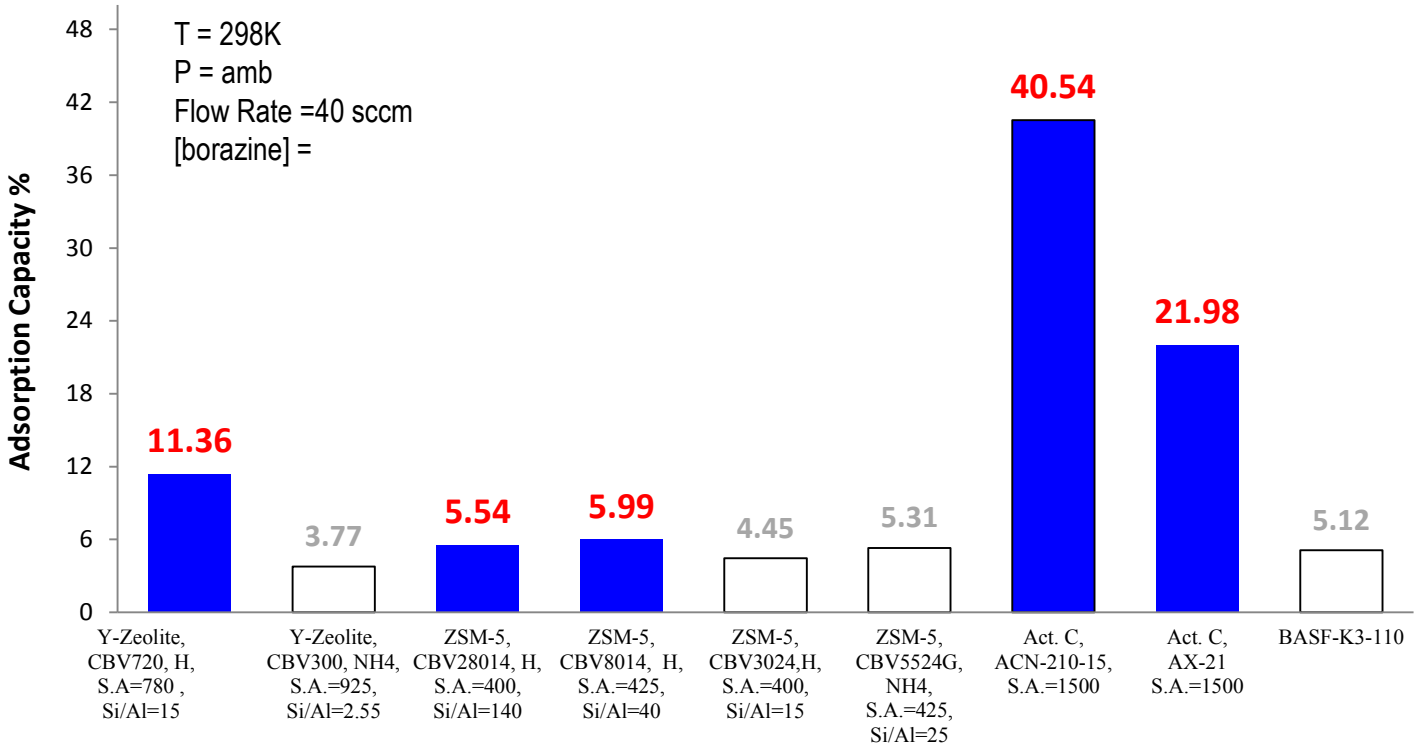
Borazine Adsorbents

Sample group	Sample name/ID	Form	Surface acidity (Si/Al)	Surface area (m^2/g)	Av. Particle size (µm)
Y-zeolite	CBV720	H	15	780	<461
	CBV300	NH_4	2.55	925	<461
ZSM-5 (as-received)	CBV28014	H	140	400	<461
	CBV3024	H	15	400	<461
	CBV8014	H	40	425	<461
	CBV5524G	NH_4	25	425	<548
ZSM-5 (modified)	Cu/Zn on CBV3024E				
	Cu/Zn on CBV5524G	NH_4	25	270	<653
Activated carbon	ACN-210-15	Felt		1500	
	AX-21	Porous particle		1500	
	DMAP impregnated in AX-21	Porous particle			
Oxides	BASF-K3-110				
	Al_2O_3				
	SiO_2				
	ZnO				

Borazine Adsorption: Dynamic Conditions

Downselected Adsorbents:

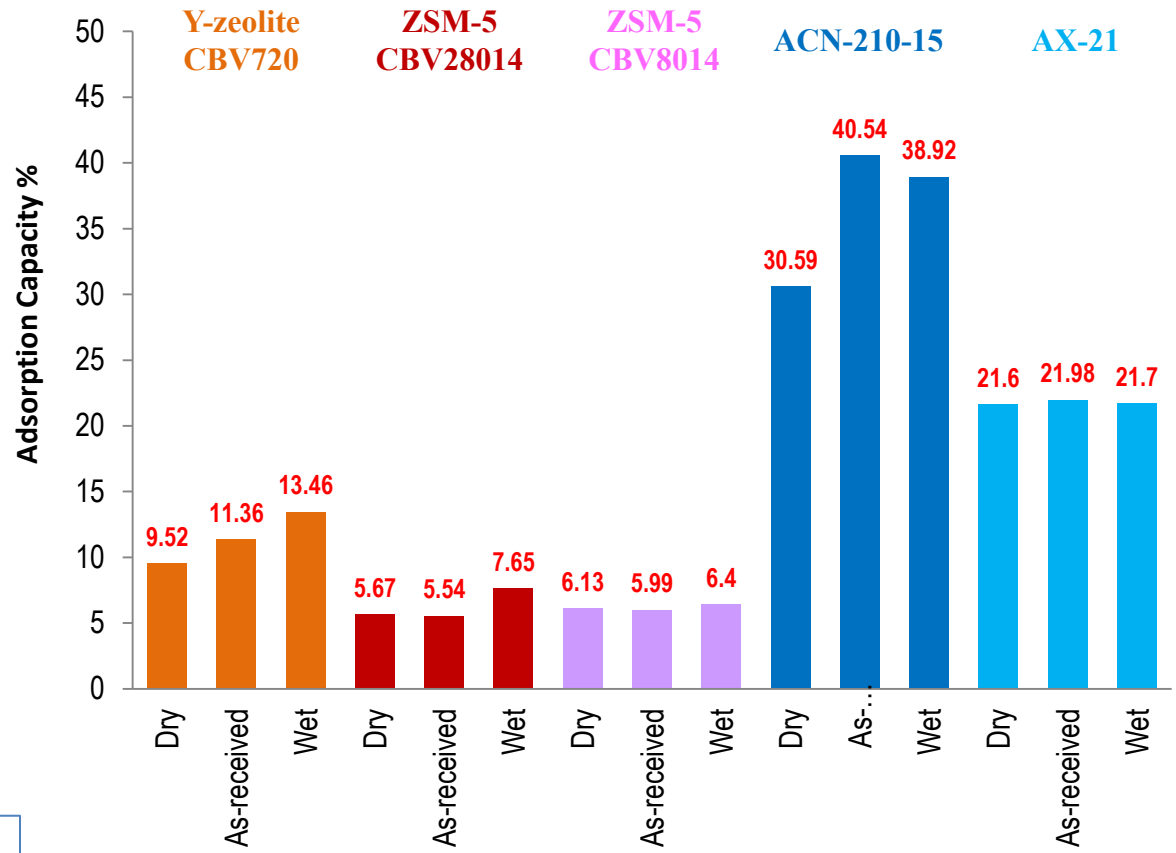
- ✓ Y-zeolite (CBV720)
- ✓ ZSM-5 (CBV28014, CBV8014)
- ✓ Activated carbon (ACN-210-15, AX-21)



$$Adsorption\ Capacity\ (\%) = \left(\frac{m_{adsorbate}}{m_{adsorbent}} \right) \cdot 100$$

Borazine Adsorption: Pre-treatment Effects

- Zeolites and AX-21 demonstrated only slight differences in borazine adsorption capacities as a function of pre-treatment
- ACN-210-15 demonstrated improved adsorption capacity as a function of humidification
  - Down selected for further study



Note: Chemically modified ACN did not show marked improvements in borazine adsorption or polymerization capacities

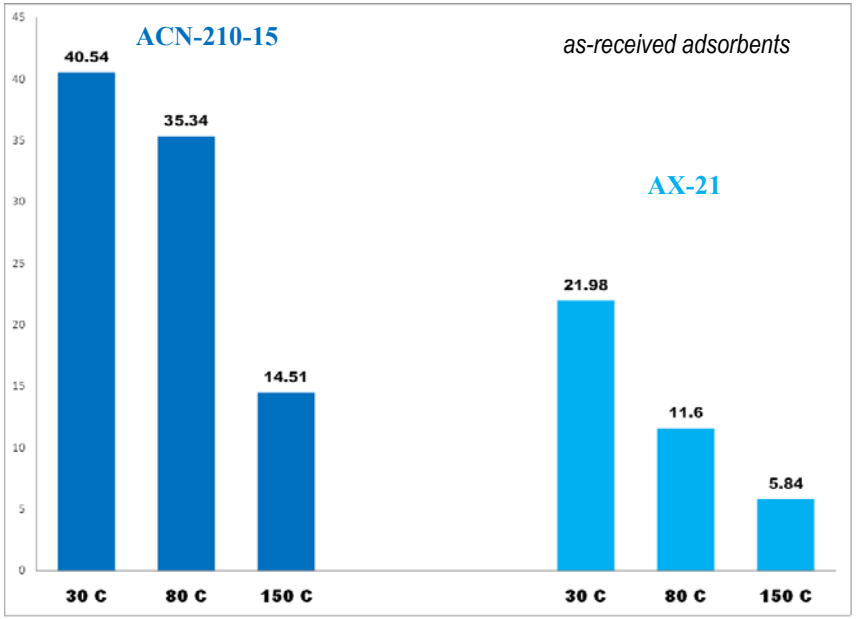
T = 298K
P = amb
Flow Rate = 40 sccm
[borazine] =

Humidifying Conditions: samples were exposed to a saturated water stream for two hours prior to adsorption experiments

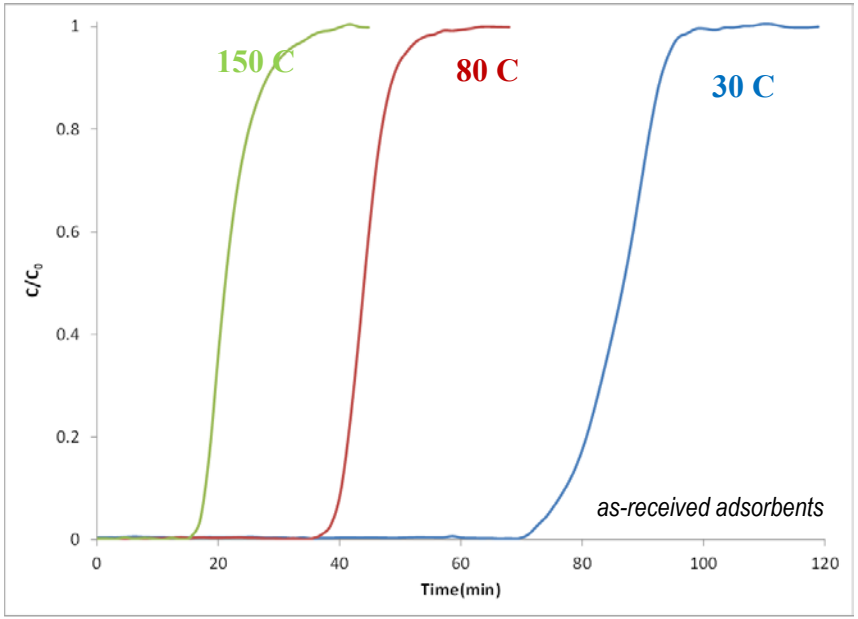
Drying Conditions: Dried @ 350 C for > 12 hr under Ar flow

Borazine Adsorption: Temperature Effects

Adsorption capacity as a fcn of temperature



Borazine breakthrough curves for ACN-210-15

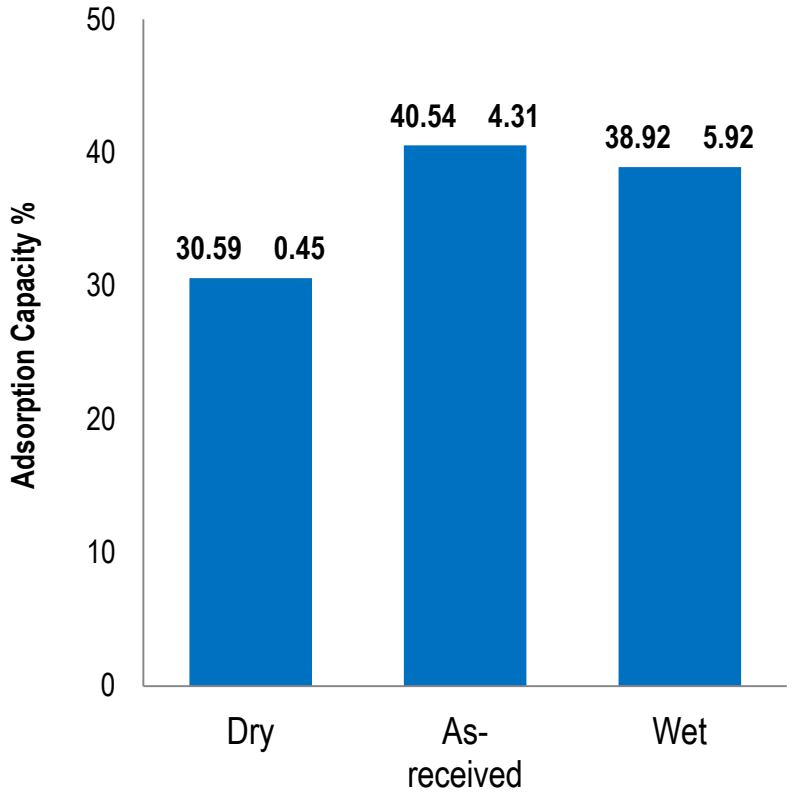


$$Adsorption\ Capacity\ (\%) = \left(\frac{m_{adsorbate}}{m_{adsorbent}}\right) \cdot 100$$

$$\uparrow Temperature\ =\ \downarrow Adsorption\ Capacity\ (\%)$$

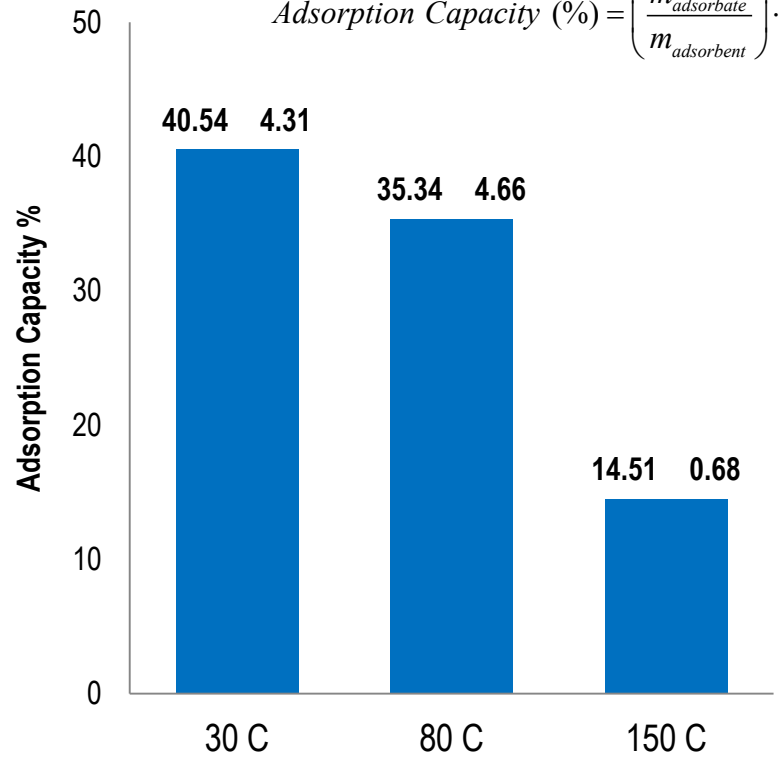
Borazine adsorption capacity with ACN-210-15

Adsorption capacity as a fcn of sample pre-treatment



Adsorption capacity as a fcn of temperature

$$Adsorption\ Capacity\ (\%) = \left(\frac{m_{adsorbate}}{m_{adsorbent}}\right) \cdot 100$$



$$(as-received) \approx (wet) > (dried)$$

$$\uparrow Temperature = \downarrow Adsorption\ Capacity\ (\%)$$

Ammonia-Borazine Competitive Adsorption

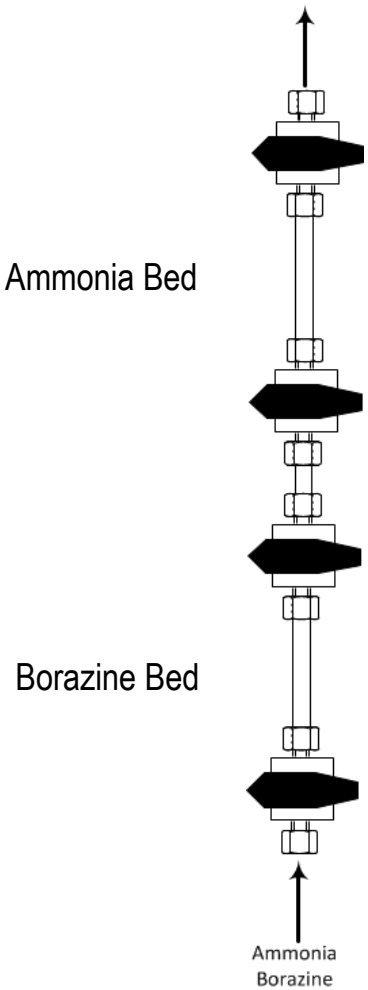
Adsorbents

✓Borazine Adsorbent: ACN-210-15
✓Ammonia Adsorbent: $MnCl_2$ /IRH-33 (UTRC supplied)

Approach

✓Competitive adsorption:
NH_3 and borazine co-fed into
(i) ACN-210-15
(ii) $MnCl_2$ / IRH-33

✓Combining adsorption beds in series:
Co-feed NH_3 and borazine through the borazine and ammonia adsorption beds connected in series



Competitive Adsorption ACN-210-15

Borazine Adsorption Capacity: ACN-210-15

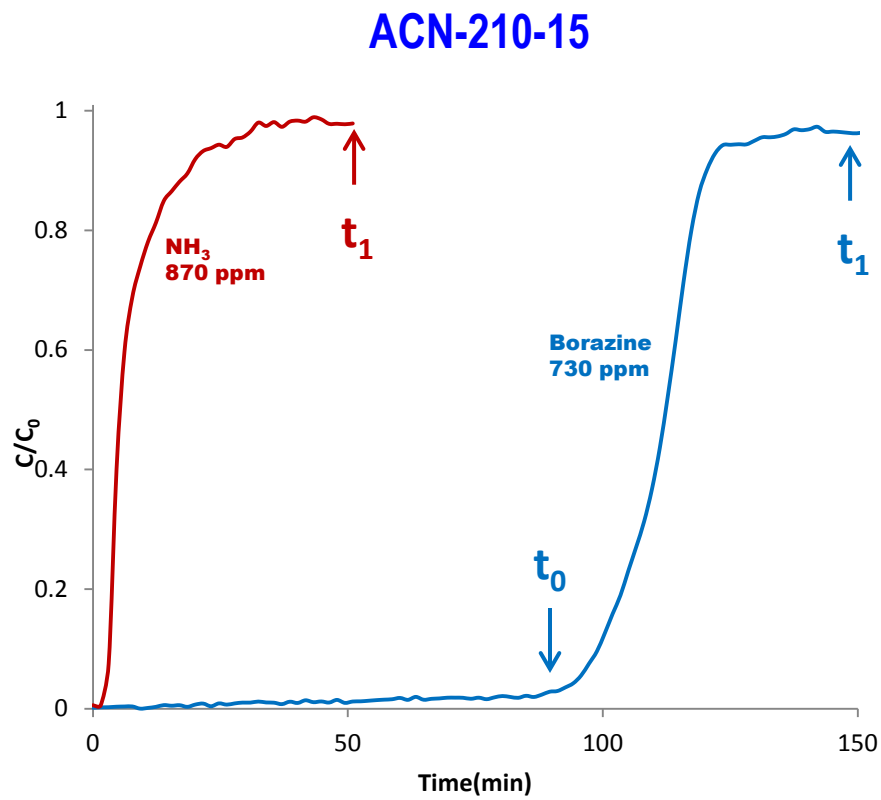
$$\left(Ads\ Capacity\right)_{Borazine}\Big|_{0}^{t_1} \approx 40\%$$

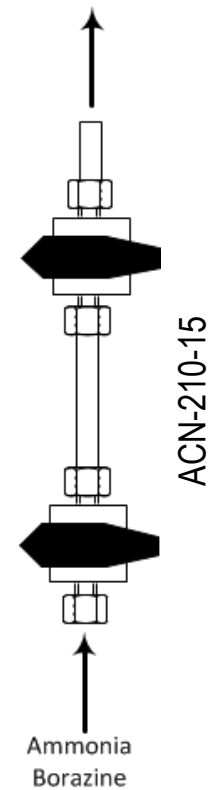
$$\left(Ads\ Capacity\right)_{Borazine}\Big|_{0}^{t_0} \approx 33\%$$

Ammonia Adsorption Capacity: ACN-210-15

$$\left(Ads\ Capacity\right)_{Ammonia}\Big|_{0}^{t_1} \approx 1\%$$

$$\left(Ads\ Capacity\right)_{Ammonia}\Big|_{0}^{t_0} \approx 0.3\%$$





Ammonia has a low adsorption capacity in ACN-210-15

Competitive Adsorption $MnCl_2$/IRH-33

Borazine Adsorption Capacity: $MnCl_2$/IRH-33

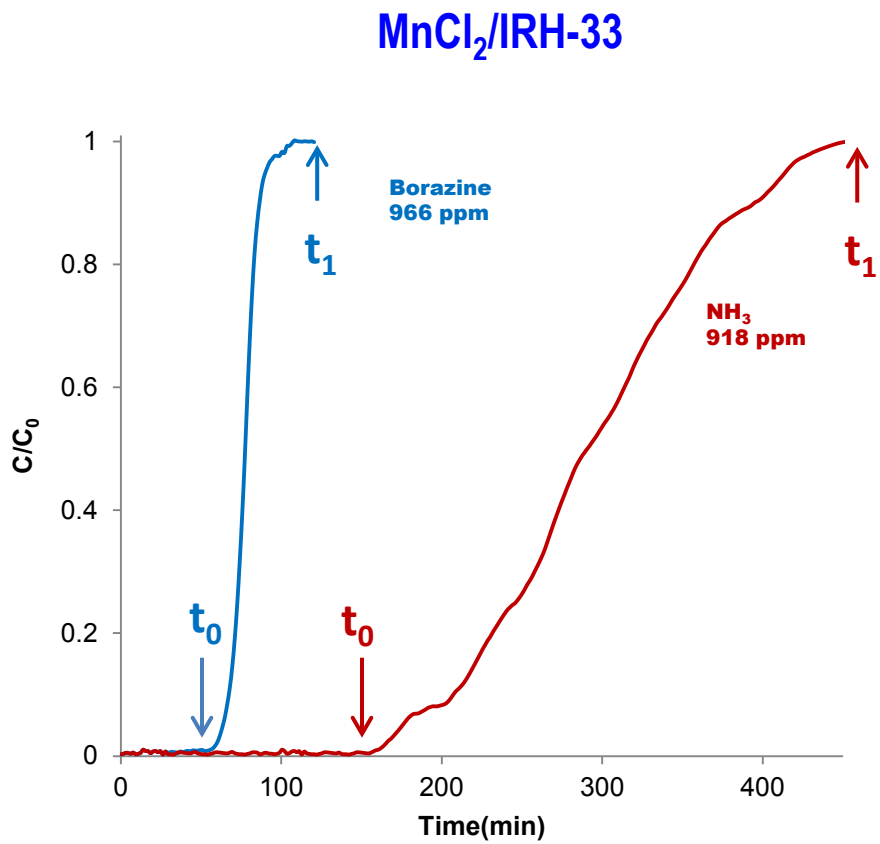
$$(Ads\ Capacity)_{Borazine}\Big|_0^{t_1} \approx 6\%$$

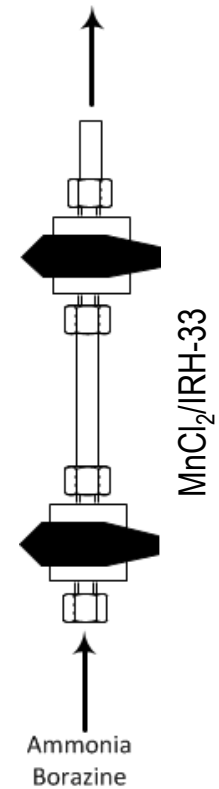
$$(Ads\ Capacity)_{Borazine}\Big|_0^{t_0} \approx 5\%$$

Ammonia Adsorption Capacity: $MnCl_2$/IRH-33

$$(Ads\ Capacity)_{Ammonia}\Big|_0^{t_1} \approx 6\%$$

$$(Ads\ Capacity)_{Ammonia}\Big|_0^{t_0} \approx 3\%$$





Ammonia and Borazine have comparable chemical affinities in $MnCl_2$/IRH-33

Order of beds should be ACN-210-15 followed by $MnCl_2$/IRH-33

Purification of Ammonia & Borazine

Borazine Adsorption Capacity

$$(Ads\ Capacity)_{Borazine}\Big|_0^{t_1} \approx 40\%$$

$$(Ads\ Capacity)_{Borazine}\Big|_0^{t_0} \approx 33\%$$

Ammonia Adsorption Capacity

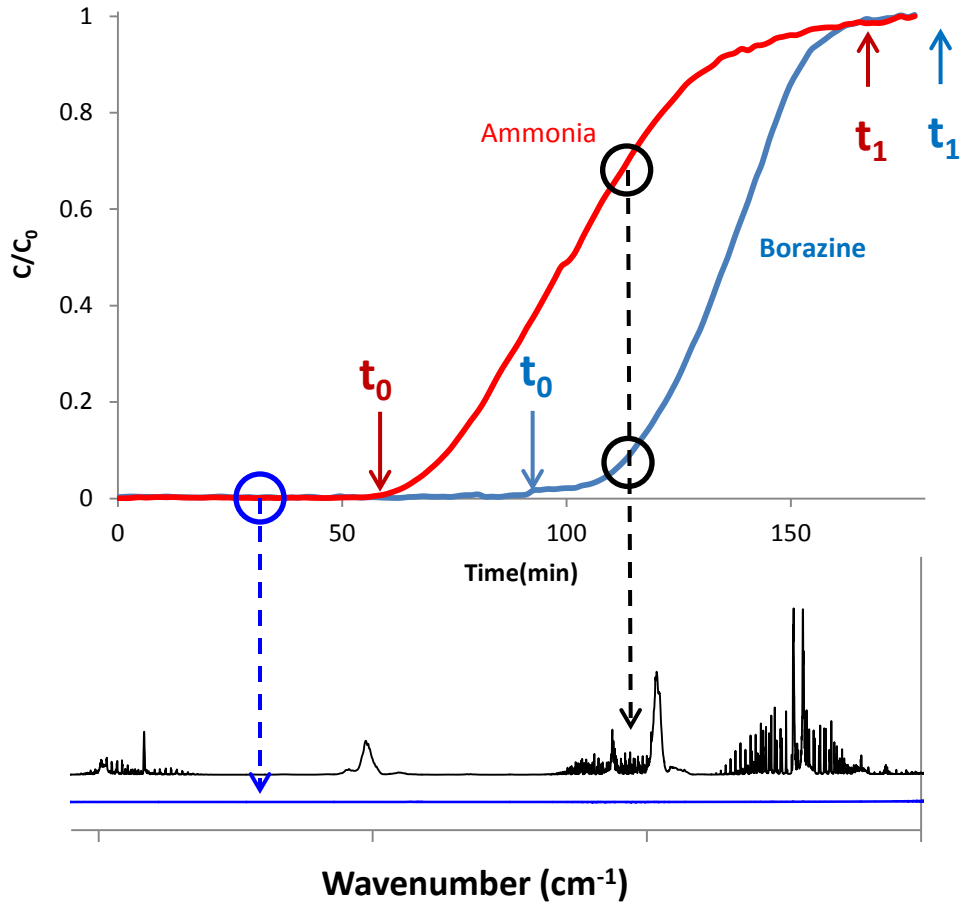
$$(Ads\ Capacity)_{Ammonia}\Big|_0^{t_1} \approx 10\%$$

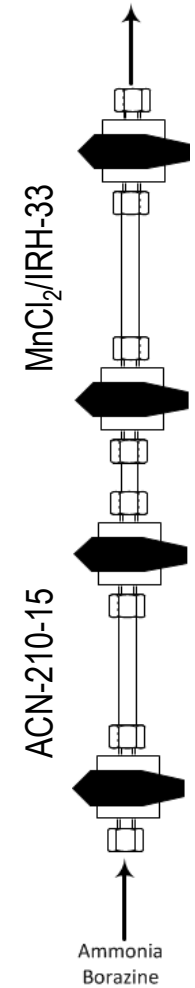
$$(Ads\ Capacity)_{Ammonia}\Big|_0^{t_0} \approx 7\%$$

Adsorbed Masses:

$Borazine \approx 23\ mg$

$Ammonia \approx 30\ mg$





Demonstrated that ammonia and borazine can be scrubbed to produce fuel-cell grade hydrogen

Conclusions

- **ACN-210-15 demonstrated the highest borazine adsorption capacity at ~ 40%**

ACN-210-15> AX-21> Y-zeolite > ZSM-5 > Oxides

Note: Chemically modified substrates did not show marked improvements over the as-received analogs

- **ACN-210-15 is an off-the-shelf carbon adsorbent requiring no special pretreatments or handling**
- **ACN-210-15 is a woven felt that is ideally suited for vibration prone environments because ACN-210-15 is not friable**
- **Adsorption capacity decreases with increasing temperature**
- **Borazine has higher chemical affinity toward $MnCl_2$ than ammonia has for ACN-210-20**

Purification order is important: borazine needs to be scrubbed prior to ammonia