



**Hydrogen Storage Engineering**  
CENTER OF EXCELLENCE

# Chemical Hydride Rate Modeling, Validation, and System Demonstration

## LANL Team

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***DOE Fuel Cell Technologies Program Annual Merit Review,  
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program  
Washington, DC June 09-13, 2011  
Technology Development Manager : Ned Stetson***



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**Project ID: ST007**

# LANL Project Overview

## Timeline

- Project Start Date: Feb FY09
- Project End Date: FY14
- Percent Complete: 38%

## Budget

- Project End Date: FY14
- Funding:
  - 2009: \$578K
  - 2010: \$712K
  - 2011: \$600K

## Barriers

### • Barriers Addressed

- *Efficiency*
- *Gravimetric Capacity*
- *Volumetric Capacity*
- *Durability/Operability*
- *H<sub>2</sub> Discharging Rates*
  - *Start time to full flow*
  - *Transient Response*
- *H<sub>2</sub> Purity*
- *Environmental, Health & Safety*

## 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			

# HSECoE Partners



# LANL Management Accomplishments/Highlights

## ➤ Technology Area Team Lead for:

- **Chemical Hydrogen Storage Properties:** *Gathered pertinent thermo-physical properties and identified missing property data for chemical hydrides and identified institution for quantifying necessary data*
- **Sensors:** *Developed a first generation fuel gauge sensor that also monitors tank integrity*
- **System Design Concepts and Integration:** *Delivered preliminary design concepts*
  - *Solid-phase chemical hydrogen storage (PNNL developed)*
  - *Fluid-phase chemical hydrogen storage (LANL developed)*

## ➤ Chemical Hydrogen Storage Liaison

- Chemical Hydrogen Storage Researchers
- Hydrogen Storage Tech Team
- Hydrogen Safety Panel
- Hydrogen Production & Delivery Tech Team

## ➤ Chemical Hydrogen Storage **System Architect & Fluid-Phase System Designer**

✓ *Monitored progress on chemical hydrides technology across the technology areas for needed features to be advanced and to insure needed communication across groups and areas occurs*

✓ **Assessed system for ECoE Phase 1 to Phase 2 Transition:**

- *Assessment performed on solid AB (PNNL system design)*
- *Assessment performed on fluid-phase AB (LANL system design)*

# LANL Engineering Tasks in Support of HSECoE

## LANL Engineering Tasks (Presentation Order)

### Task 7: Design, Build, and Demonstrate a Subscale Prototype System

Task7a: Design automotive-scale systems

Task 7b: Design and build bench-scale validation test bed

### Task 2: Develop Fuel Gauge Sensors for Hydrogen Storage Media (*Ahead of Schedule*)

### Task 6: Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies (*On Schedule*)

### Task 4: Develop Rate Expressions of Hydrogen Release for Chemical Hydrides (*On Schedule*)

### Task 5: Develop Novel Reactor Designs for Start-up and Transient Operation for Chemical Hydrides (*On Schedule*)

### Task 3: Develop Models of the Aging Characteristics of Hydrogen Storage Materials (*Effort reduced due to funding constraints*)

# Task 7a: LANL Fluid Phase System Designs

## ✓ Relevance:

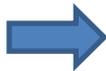
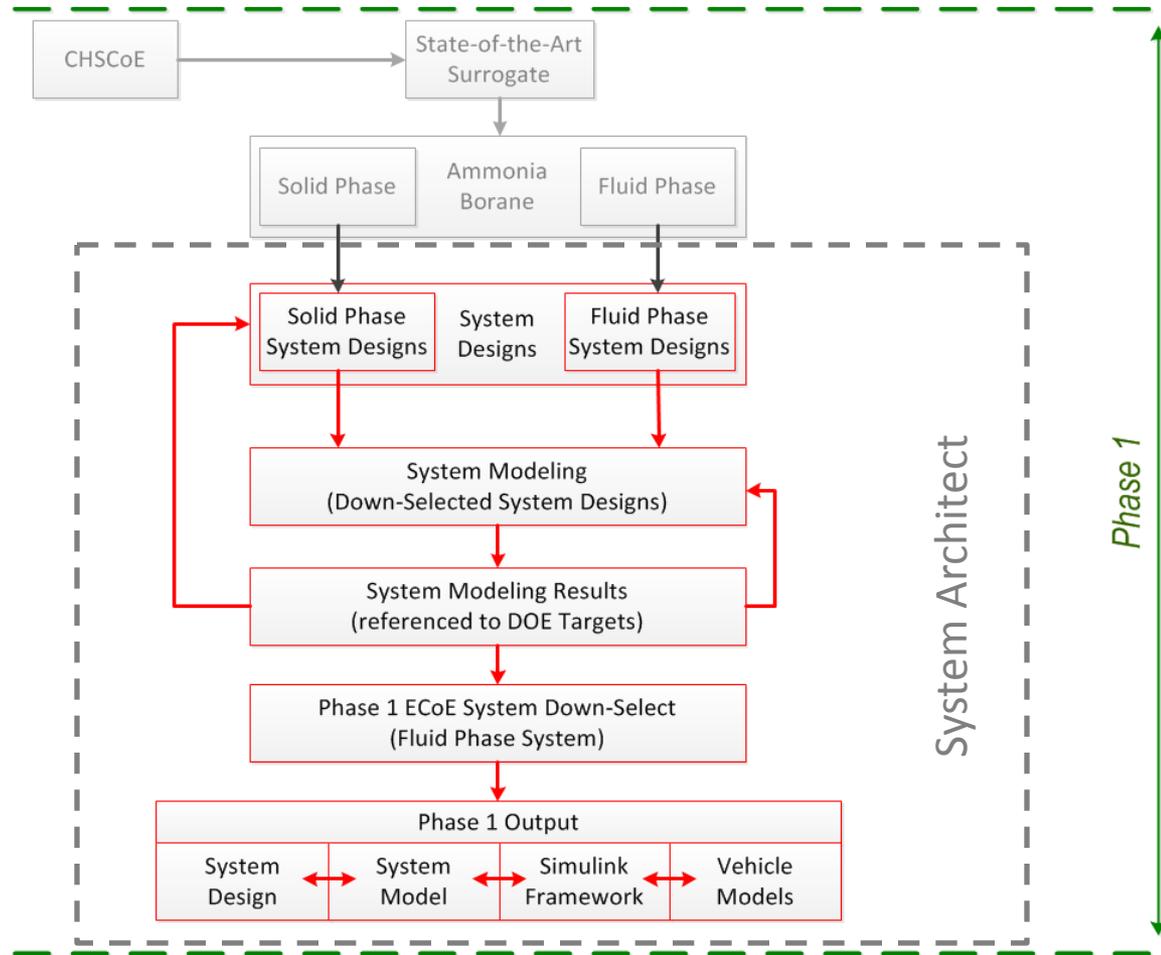
- Automotive scale fluid-phase chemical hydrogen storage system
- Ultimate Goal of the DOE
- 2015 DOE Targets Addressed: All

## ✓ Expected Outcomes:

- System level design
- Identified areas requiring novel R&D approaches
- System design for modeling purposes

## ✓ Task/Approach:

- 7a.1 Design fluid-phase CHS system
- 7a.2 When possible use off-the-shelf BOP components



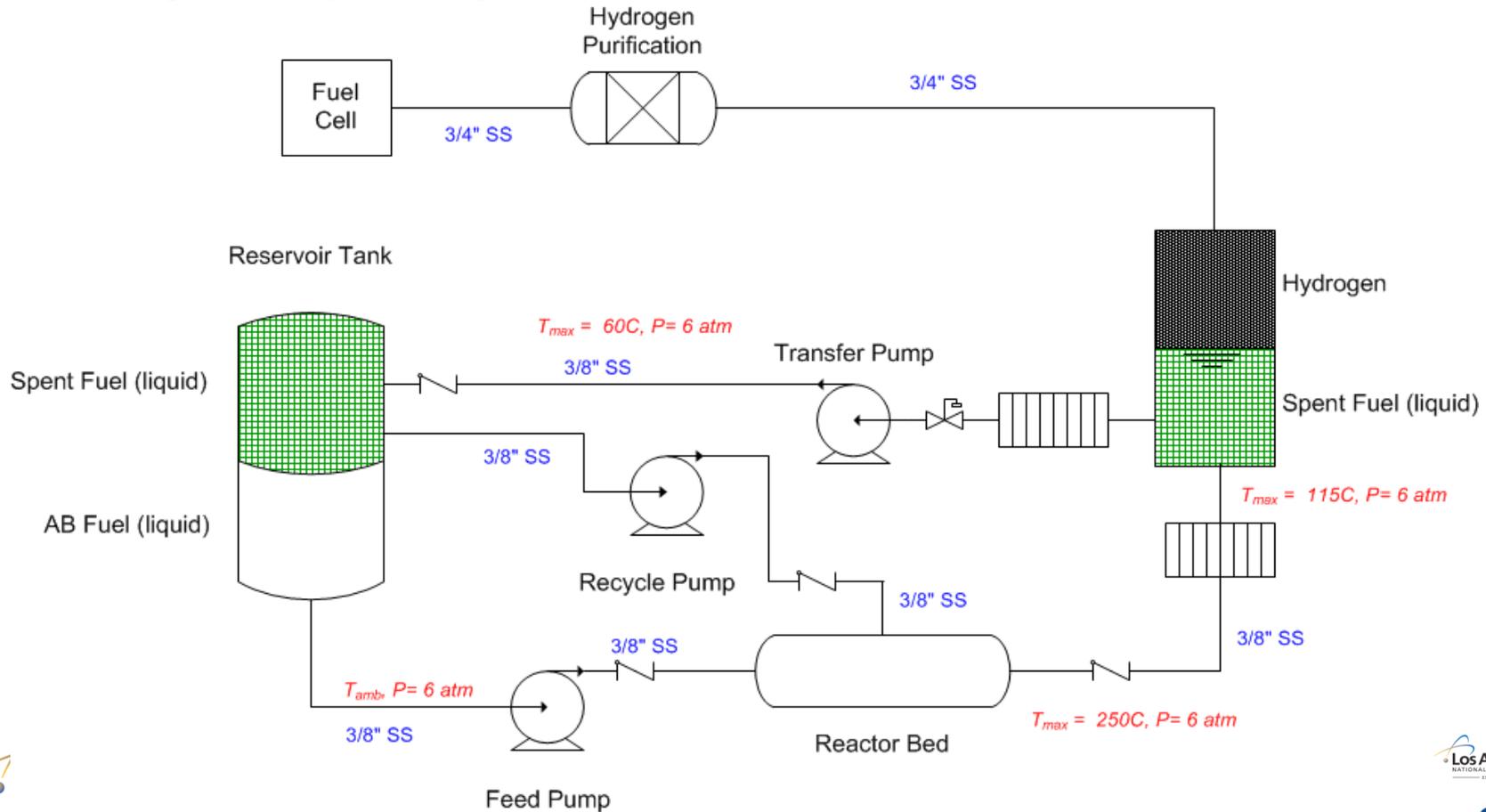
# Task 7: LANL Fluid Phase System Designs

## Unit Operations of Fluid-Phase AB System

- Dehydrogenation Reactor (*Transport*)
- Gas-Liquid Separator (*Enabling Technologies, Transport*)
- Hydrogen Purifier (*Enabling Technologies*)
- Heat Exchanger (*Enabling Technologies*)

## BOP Components of Fluid-Phase AB System

- Pumps
- Storage Tank(s) (*Enabling Technologies*)
- Fuel/Spent Fuel
- Ballast Tank



# Task 7: LANL Fluid Phase Preliminary System Design

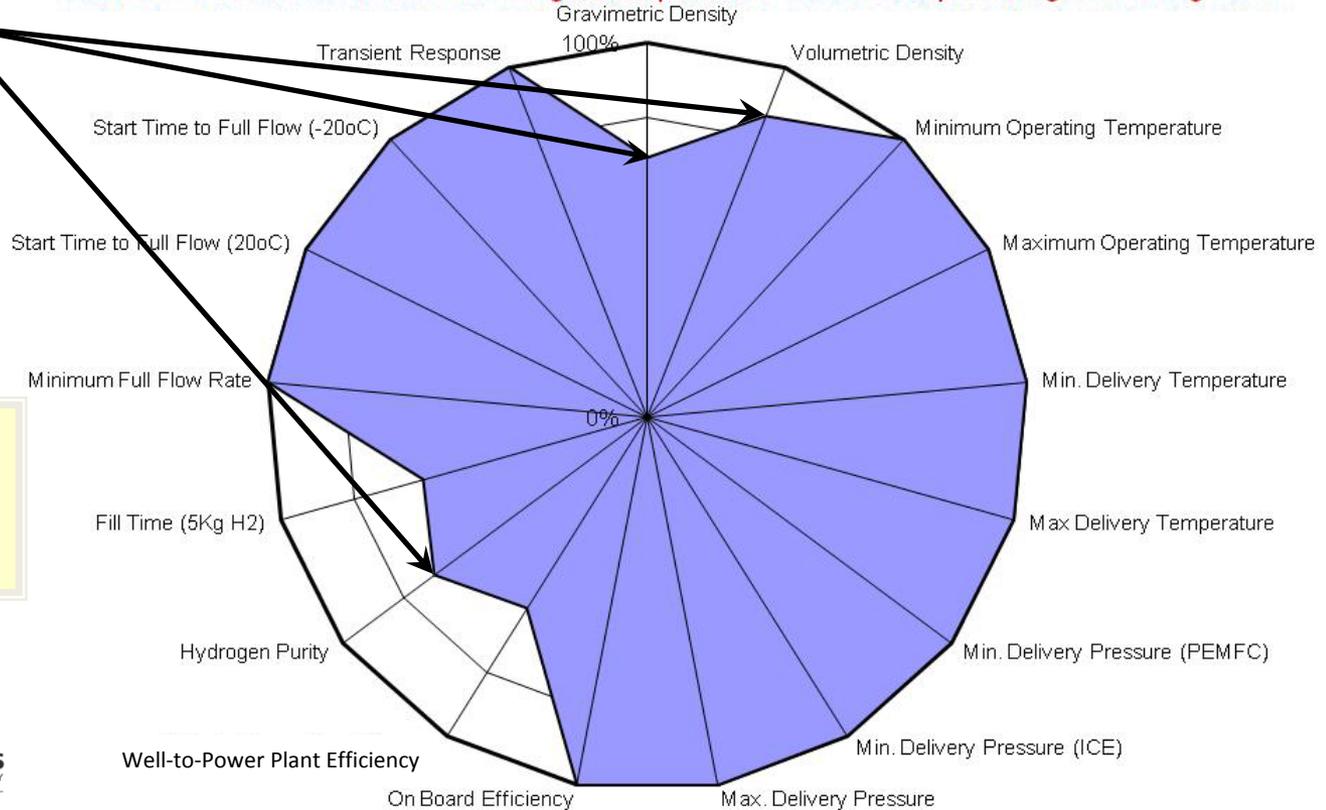
1. Gravimetric Ratio
2. Volumetric Density
3. Hydrogen Purity
4. WTPP Efficiency<sup>a</sup>
5. Fill Time<sup>b</sup>

- <sup>a</sup> Not within the ECoE Research Scope
- <sup>b</sup> Target met if emptying and filling are performed simultaneously (2.7 min)

- 13 DOE 2015 Targets Fully Met
- 4 Targets above 60+%

## DOE 2015 Targets for Liquid Ammonia Borane Flow Through System

NOTE: All metrics that exceed DOE targets are plotted at 100% to keep the diagram scaling intact

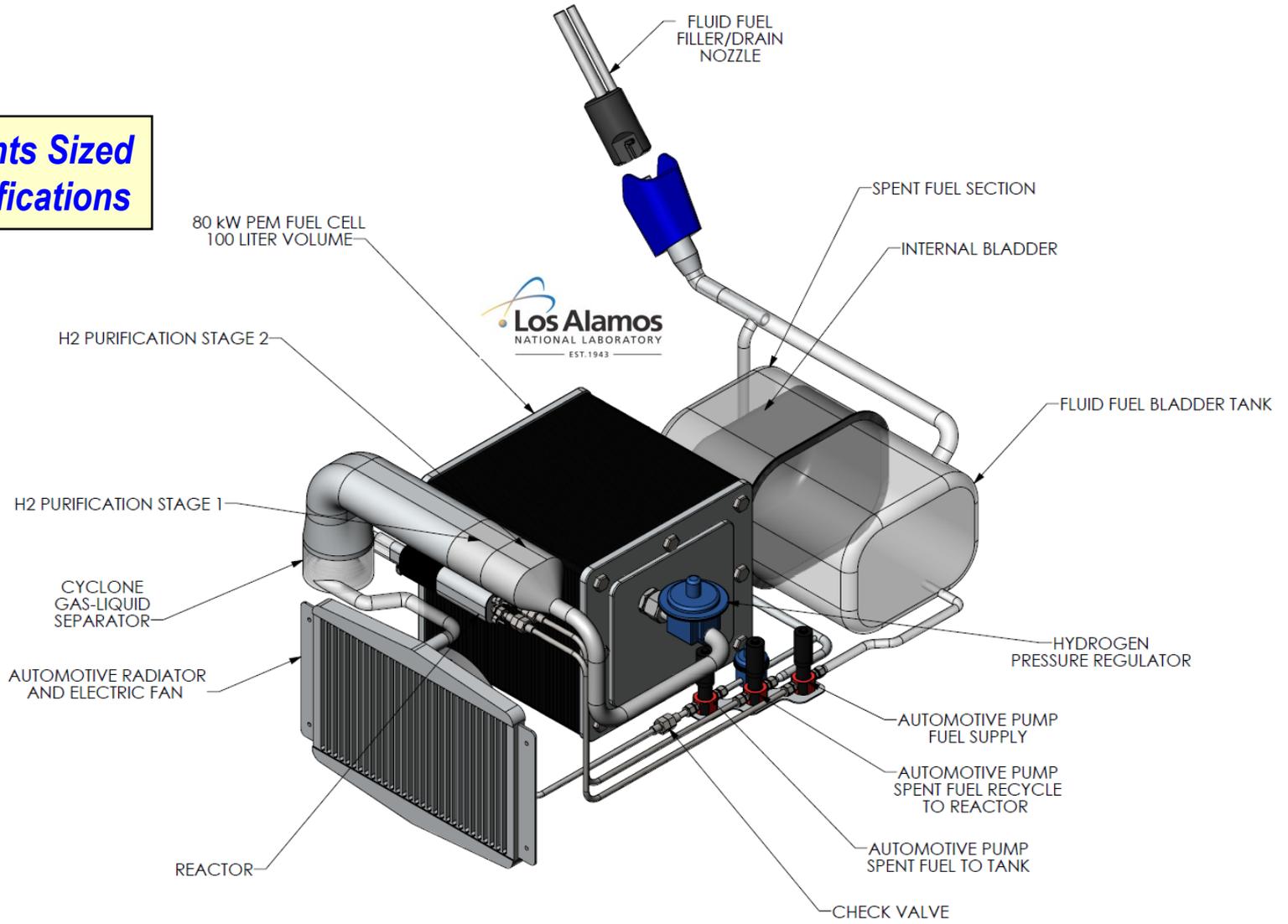


Note: DOE Targets Fuel Cost, System Cost, & Cycle Life were left off of the Spider Chart



# Task 7: LANL Liquid Phase Preliminary System Design

**All Components Sized  
to BOP Specifications**



# Task 7a Summary and Future Work: System Designs

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## Summary

- Developed many system design concepts for fluid-phase chemical hydrogen storage media (surrogate is fluid-phase AB)
- Provided preliminary system design to PNNL, NREL, and UTRC for modeling purposes
  - Sizing, temperatures, pressures, conversions, etc.
- Provided off-the-shelf components to PNNL for BOP costing
- Developed novel reactor, gas-liquid separator, and hydrogen purification train (unproven concepts)
- LANL fluid-phase chemical hydrogen storage system design down-selected based on 2015 DOE targets as the priority for Phase 2

## Future Work

- Continue to refine system design (and models) as needed based on experiment validation experiments
- Identify, develop, and implement novel system components
- Update experimental setup and protocols as needed to ensure accurate data for model development

# Task 7b: LANL Fluid-Phase Validation Test Bed

## ✓ Relevance:

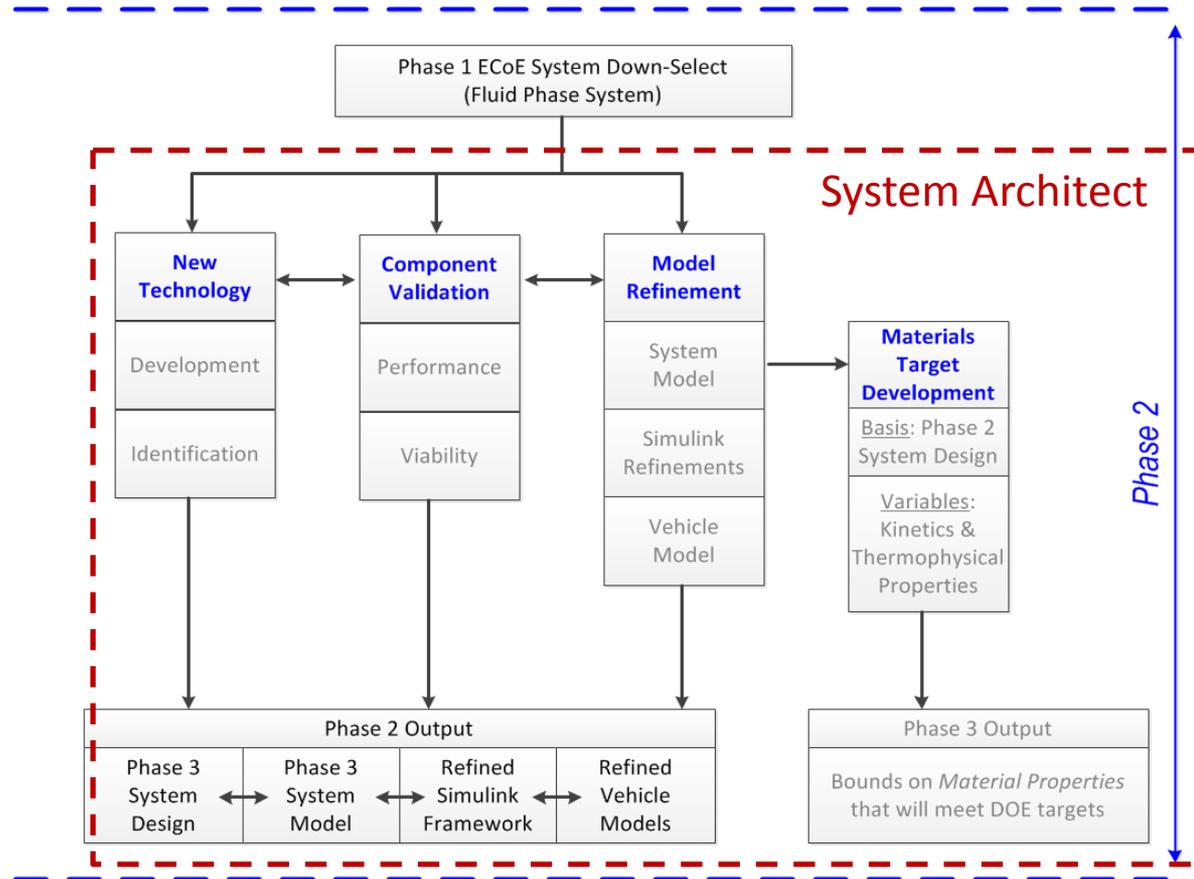
- Component validation (performance and viability)
- System validation (system integration)
- Model refinement
- System refinement

## ✓ Expected Outcomes:

- Modular test bed for validating individual components or systems
- Test bed for acquiring kinetics (Task 4), impurities (Task 6), and reactor performance (Task 5)

## ✓ Task/Approach:

- 7a.1 Design fluid-phase CHS system
- 7a.2 When possible use off-the-shelf BOP components
- 7a.3 Identify components that require novel R&D approaches



# Task 7b: LANL Fluid-Phase Validation Test Bed

## Fluid Phase System Component Validation Setup

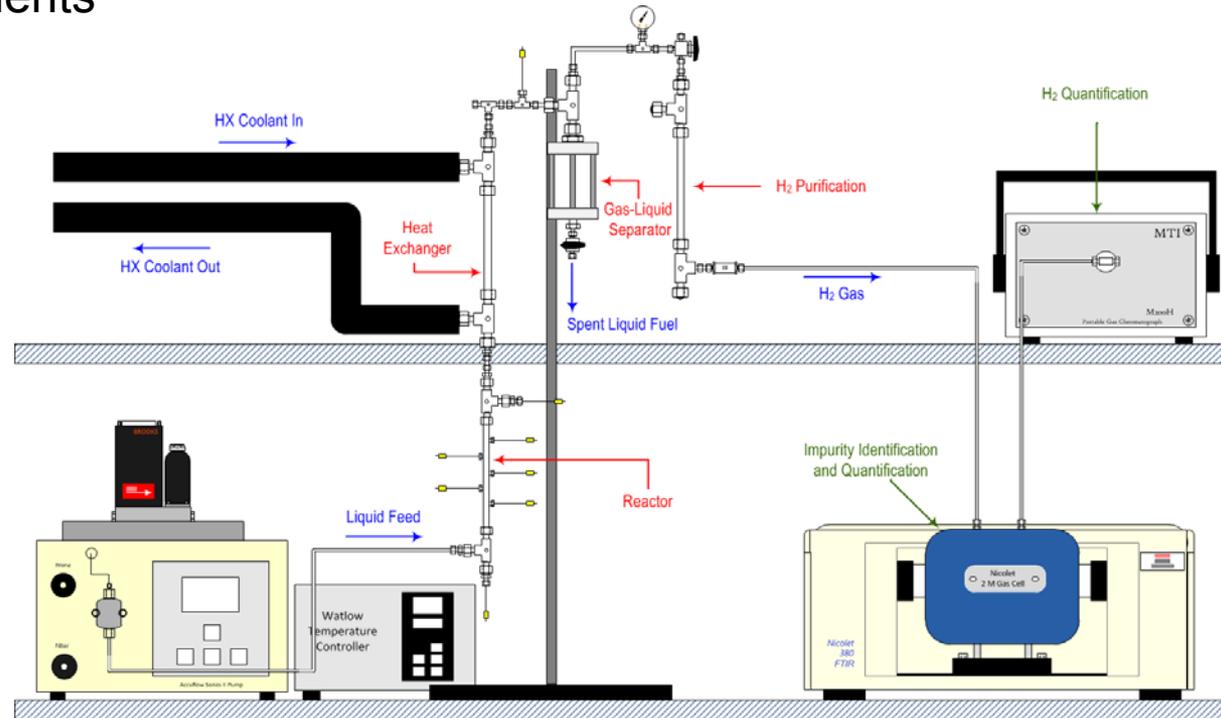
### Deployed for Phase 2 Activities

#### 1. Validate System Components and Technology

- Reactors
- Gas-Liquid Separators
- $H_2$  Purification

#### 2. Validate and Refine System Models

#### 3. Optimize System Designs

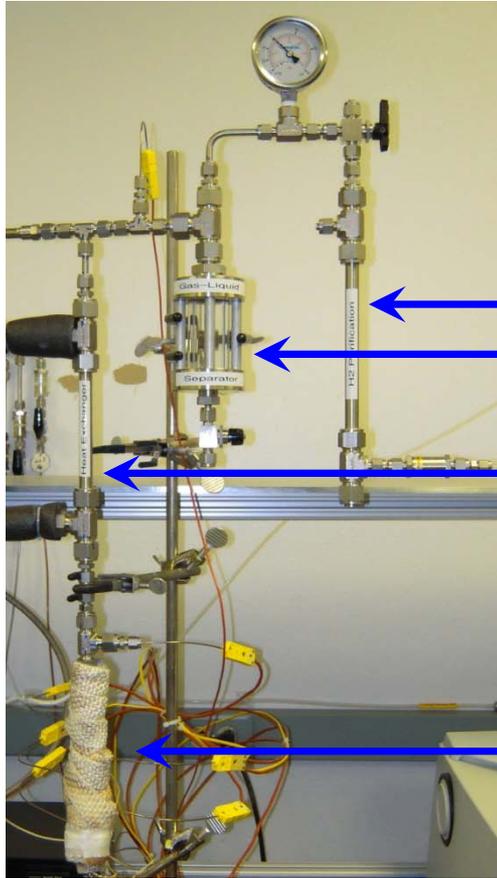


**Phase 2 Ready and Adaptable to any Fluid**



# Task 7b: LANL Fluid-Phase Validation Test Bed

- Fluid Phase Chemical Hydride System Component Validation Setup

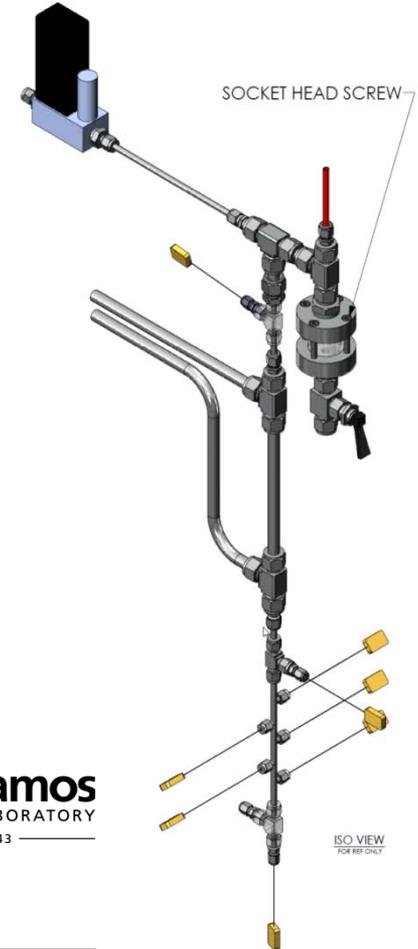


H<sub>2</sub> Purification

Gas-Liquid Separator

Heat Exchanger

Reactor



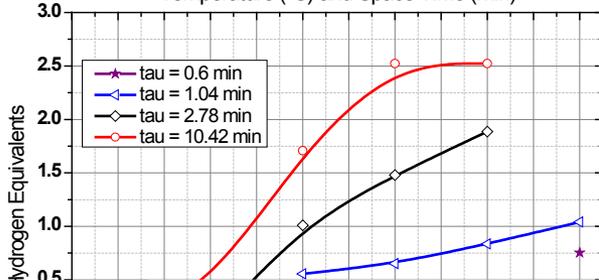
*Modular Design Allows for Validating Individual System Components or Integrated Systems*



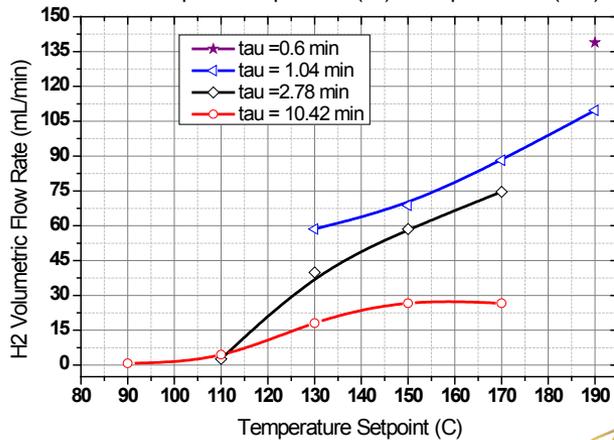
# Task 7b: LANL Fluid-Phase Validation Test Bed

- Kinetics Results from Using Fluid Phase AB as a H<sub>2</sub> Source

Plot of H<sub>2</sub> Equivalents produced as a function of Reactor Setpoint Temperature (°C) and Space Time (min)



Plot of Hydrogen Volumetric Flow Rate as a function of Reactor Setpoint Temperature (°C) and Space Time (min)

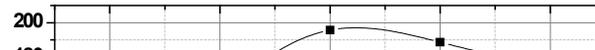


Zeolite Scrubber used for H<sub>2</sub> Purification



- Axial Temperature Profiles Observed from Using Fluid Phase AB as a H<sub>2</sub> Source

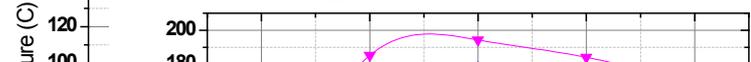
Axial Temperature Profiles within Heated Reactor Length @ r = 0 for Space time = 0.6 min



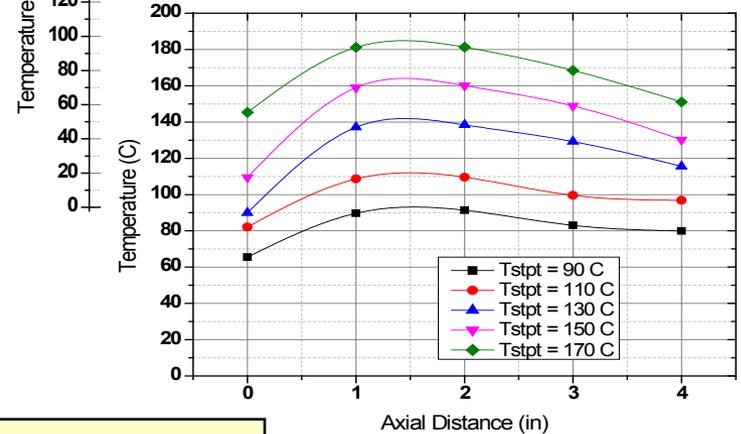
Axial Temperature Profiles within Heated Reactor Length @ r = 0 for Space time = 2.78 min



Axial Temperature Profiles within Heated Reactor Length @ r = 0 for Space time = 1.04 min



Axial Temperature Profiles within Heated Reactor Length @ r = 0 for Space time = 10.42 min



**Fluid-Phase Reactor Test Bed Validated**



# Task 7b Summary and Future Work: Test Bed

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## Summary

- Designed, built, and validated bench-scale fluid-phase chemical hydrogen validation test bed
  - Modular approach to validate individual components or integrated systems
  - Validate and refine system level models

## Future Work

- Begin validating (via experiments) system-level modeling assumptions
- Validate novel component designs for performance and viability
- Provide system modelers the necessary experimental data for system-level model refinements
- Update experimental setup and protocols as needed to ensure accurate data for model development
- Test bed fixture directly aligns with Task 4, Task 5, and Task 6

# Task 2: LANL Fuel Gauge Sensor Development

## ✓ Relevance:

- DOE targets addressed: Safety
- All commercialized vehicles necessitate a fuel gauge sensor
- Health monitoring of high pressure tanks

## ✓ Expected Outcomes:

- Fuel gauge sensor for solid- and fluid-phase hydrogen storage media
- *Containment vessel health monitoring*

## ✓ Task/Approach:

- 2.1 Identify first generation fuel gauge sensors
- 2.2 Demonstrate fuel gauge sensor technology on candidate hydrogen storage media

### ❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D1	First generation fuel gauge sensor <i>(DEMONSTRATED)</i>	DOE	Q4 FY09
Phase 2	D20	Working fuel gauge sensor capable of monitoring H2 levels within +/- 5%	DOE & ECoE	Q2 FY12

### ❖ Go/No-Go

Phase	Go/No-Go	Description	Criteria*	Date
Phase 1	G1	Go/No-Go Decision on fuel gauge sensor <i>(Go)</i>	+/- 5% of H <sub>2</sub> Stored	Q4 FY10

\* all Go/No-Go decisions will be based on the most current DOE Technical Targets; the components or designs that most favorably compare to the DOE Technical Targets will be chosen

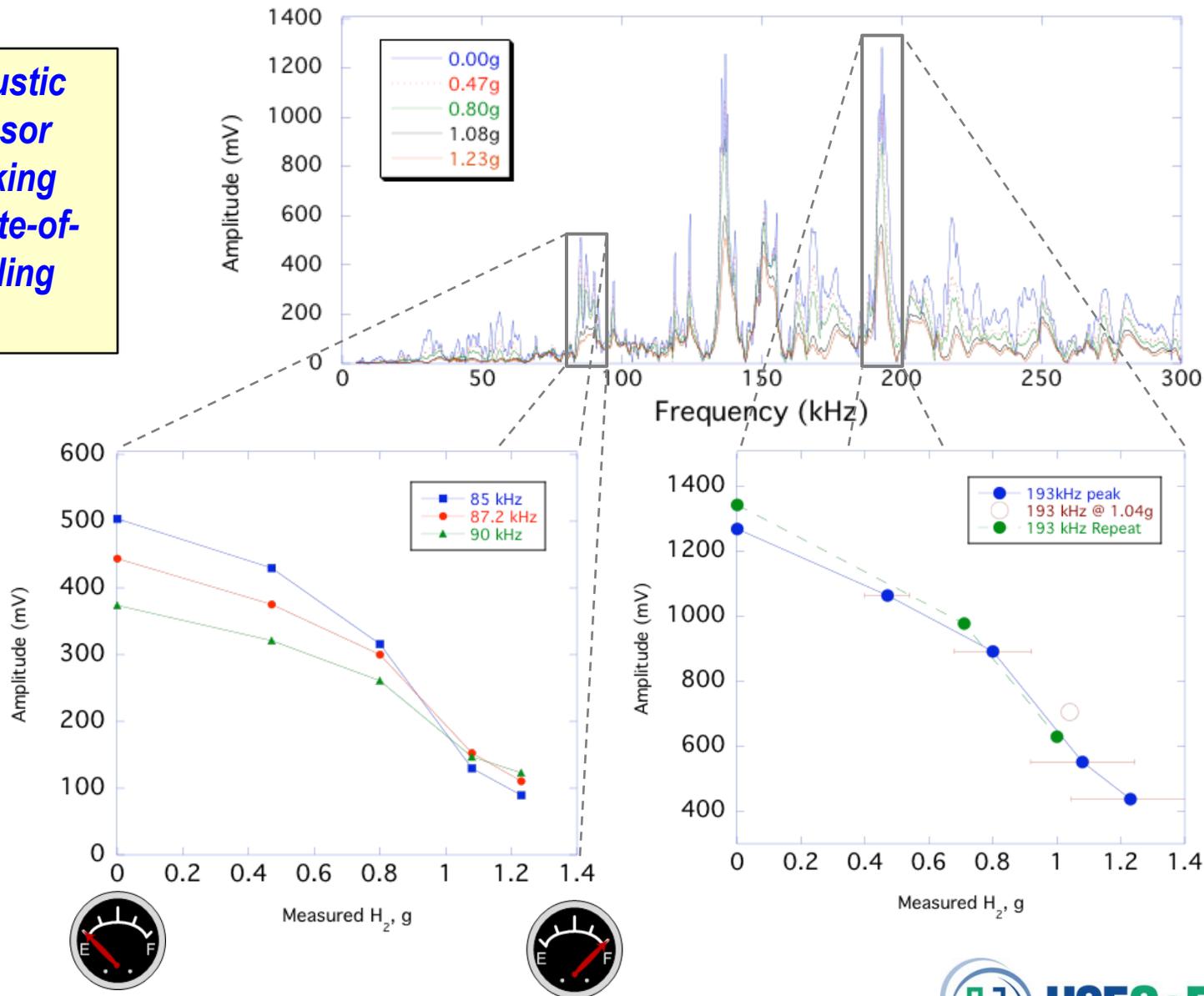
### ❖ Milestone

Phase	Milestone	Description	Dependencies	Date
Phase 2	M2	Fuel gauge sensor development and demonstration	TASK 2.1	Q3 FY11

# Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

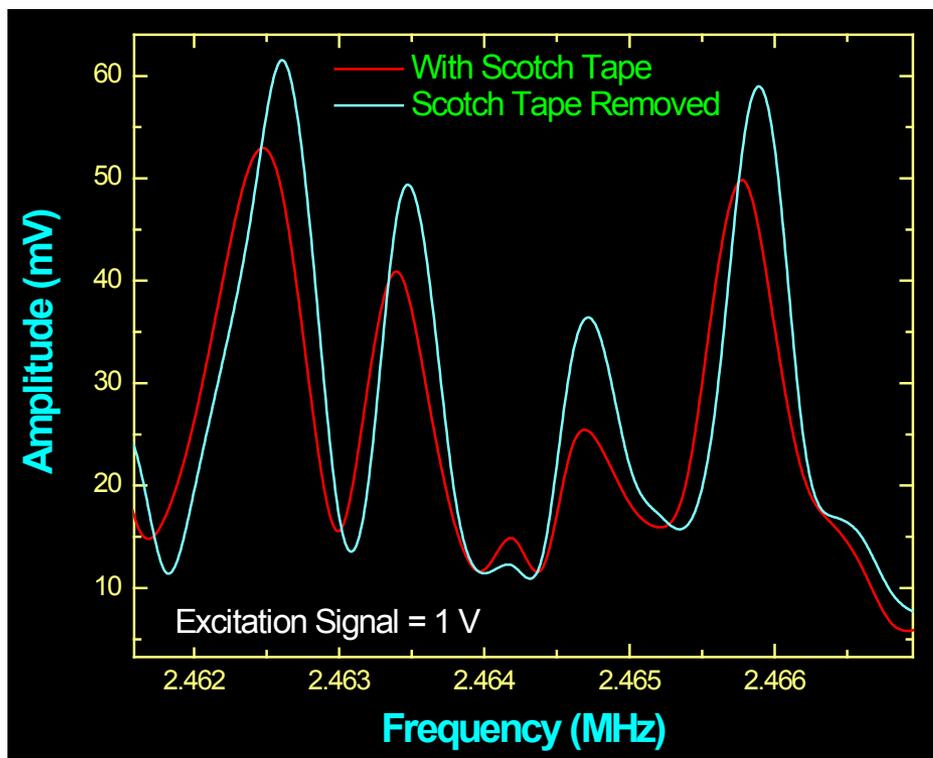
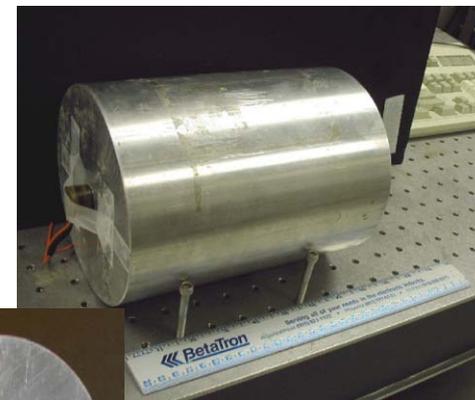
**LANL Novel Acoustic Fuel-Gauge Sensor Capable of Tracking Metal Hydride State-of-Charge and Cycling Effects**

➤ Non-evasive fuel gauge sensor



# Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

LANL Acoustic Sensor Capable of Monitoring Containment Vessel Integrity



# Task 2 Summary & Future Work: Fuel Gauge Sensor

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## Summary

- Demonstrated acoustic fuel gauge sensor proof-of-principle on various metal hydrides
- Patent Submitted
- Demonstrated acoustic fuel gauge sensor capable of tracking state-of-charge for metal hydrides
- Demonstrated acoustic fuel gauge sensor capable of monitoring the structural integrity of containment vessels (e.g. adsorbent and metal hydride systems)

## Future Work

- Finish proof-of-concept experiments for metal hydride system.
  - Permanently affix transducers to cylinder so that system may be moved for tracking state-of-charge by direct mass change measurements.
  - Cycle charge of cylinder to determine how well change in acoustic signature tracks actual H<sub>2</sub> mass changes. Measure reproducibility between charge/discharge and intermediate states.
- Start hydrogen level sensor studies for liquid AB sources.
- Start sensor studies for cryogenic adsorption hydrogen sources. Investigate methods/options available.

# Task 6: Hydrogen Impurities and Mitigation

## ✓ Relevance:

- DOE Targets Addressed:
  - Cost
  - Durability and Operability
  - Environmental, Health and Safety
  - Fuel Purity

## ✓ Expected Outcomes:

- Impurities demonstrating fuel cell degradation for all candidate storage materials
- Strategies for impurity mitigation/separation

## ✓ Tasks:

- 6.1 Identify impurities demonstrating fuel cell degradation
- 6.2 Determine adsorbate-adsorbent interactions
- 6.3 Quantify and model hydrogen impurities demonstrating fuel cell degradation
- 6.4 Identify novel impurity separation/mitigation strategies

## ✓ Go/No-Go Decision Criterion:

- DOE Technical Target of 99.99% H<sub>2</sub> purity (Q4 FY11)

❖ Deliverables	Phase	Deliverable	Description	Delivery to	Date
	Phase 1	D11	Identify fuel cell impurities	DOE, HSMCoE, & ECoE	Q4 FY10
		D12	Quantify minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY10
	Phase 2	D16	Determine fuel cell degradation via impurities	DOE & ECoE	Q4 FY11
		D17	Update on minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY11
		D23	Working Impurity mitigation device with low cost, low volume & low mass	DOE & ECoE	Q2 FY12

❖ Milestone	Phase	Milestone	Description	Dependencies	Date
	Phase 2	M4	Impurity mitigation strategy development	TASKS 6.1 and 6.3	Q1 FY11

❖ Go/No-Go	Phase	Go/No-Go	Description	Criteria	Date
	Phase 2	G2	Go/No-Go Decision on viable impurity mitigation/separation strategies	mass, volume, cost, purity	Q4 FY11

# Task 6: Hydrogen Impurities and Mitigation

Material	Onset T (°C)	Wt % ( SD)					
		NH <sub>3</sub>		Borazine		Diborane	
AB	95	2.5	0.71	3.8	0.71	1.8	0.35
Powder AB	82	2.7	0.42	2.2	0.21	0.99	0.0077
AB/MC	77	4.6	1.0	2.0	0.35	0.85	0.071

$$wt\% \equiv \frac{\text{species mass}}{\text{initial mass of AB}} \times 100$$

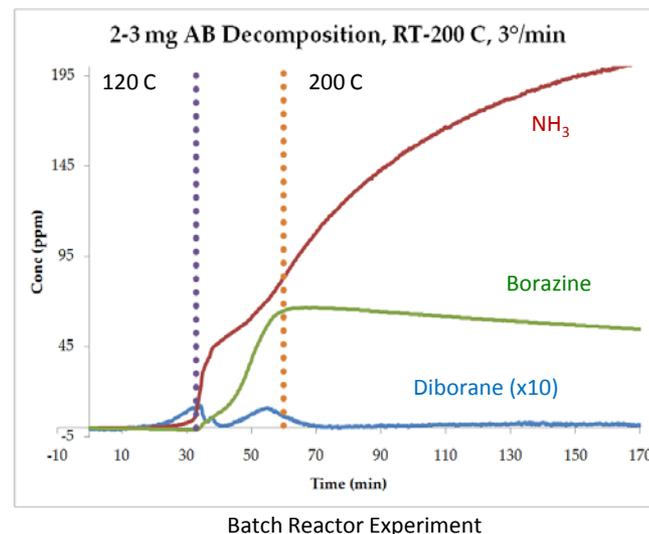
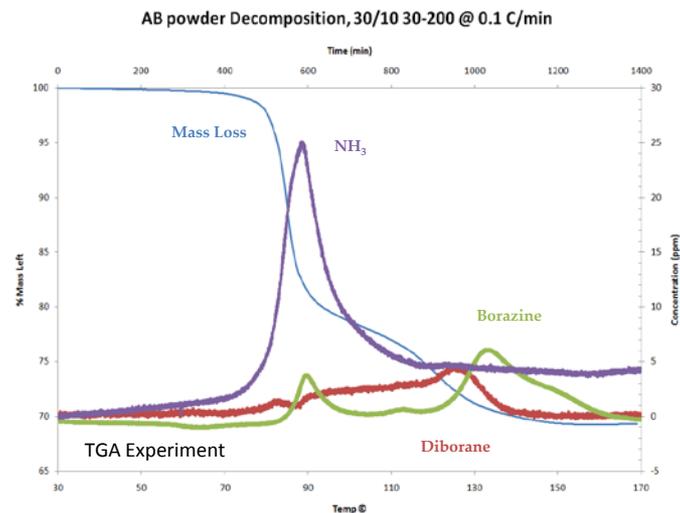
## Adsorption Media Tested

1. Ammoniasorb II
2. Selexsorb CD
3. Carbon
4. Zeolites + others

✓ Impurities can be scrubbed via adsorption media

but.....

In order to reduce mass, volume, maintenance costs, etc.. We need to address the reaction selectivity



# Task 6: Hydrogen Impurities and Mitigation

## Fuel Cell Tolerance Test with Diborane

### VI-Curve:

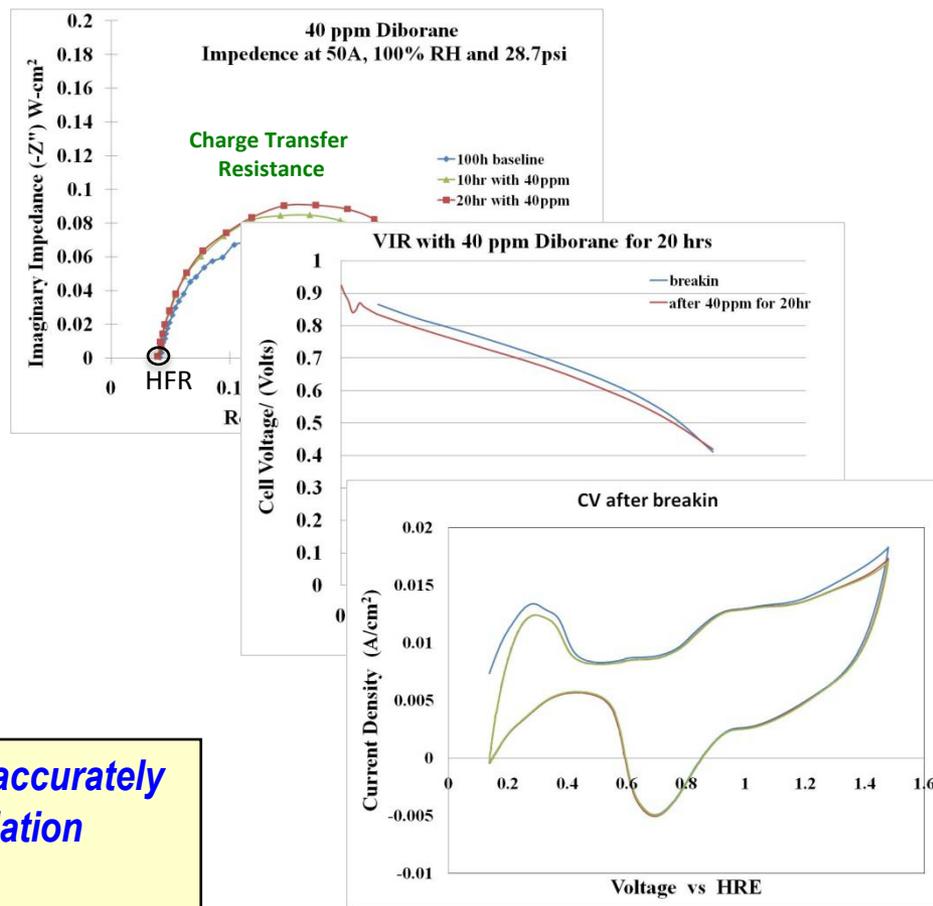
- Losses (~20mV) were observed after 20h of exposure

### AC Impedance:

- CTR increased with time**
- HFR and MTR remained constant during exposure

### Cyclic Voltammetry:

- No effect on catalyst surface area



Additional long term testing is required to accurately assess FC tolerance level and degradation mechanism

Preliminary Test Indicate Diborane Affects the Charge Transfer Resistance

A/C: 0.1/0.4 mg Pt/cm<sup>2</sup>, 100% RH, and 25 psig back pressure using 83 and 50% utilization.

# Task 6 Summary & Future Work: Impurities & Mitigation

## Summary

- Amount of impurities is a function of temperature and heating rate; mitigation strategies include increased control of reaction (i.e., thermal management, reactor design)
- Ammonia borane in current ionic liquid demonstrated a decreased production of borazine and no diborane
- Suppression of impurity generation may be achieved via catalytic routes of hydrogen release from fluid phase ammonia borane
- Borazine can be scrubbed using various adsorbents
- Preliminary fuel cell tolerance test with diborane indicate performance degradation

## Future Work

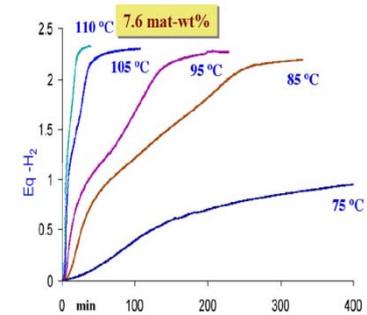
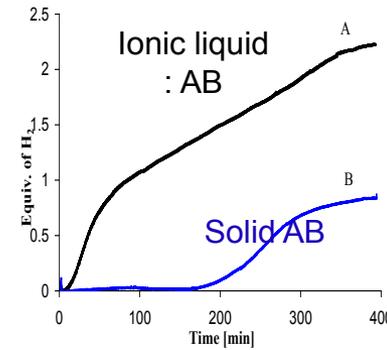
- Quantify impurities using fluid-phase bench-scale validation test bed (**TASK 7b**)
- Examine impurity mitigation strategies (i.e., catalysts, temperature control, conversion, space-time, etc.) on reaction selectivity

# Task 4: Reaction Rate Models for AB/IL Systems

- Fluid Phase AB Hydrogen Release Kinetics (Avrami-Erofeyev)

$$(r_{H_2})_{0.00}^{1.00} = 1.5 \left[ \left( 2.26056 \times 10^{17} \right) e^{\frac{-142 \text{ kJ/mol}}{RT}} \right] (1-\alpha) [-\ln(1-\alpha)]^{\left(\frac{1}{3}\right)}$$

$$(r_{H_2})_{1.00}^{2.35} = 2.5 \left[ \left( 1.09026 \times 10^{17} \right) e^{\frac{-146 \text{ kJ/mol}}{RT}} \right] (1-\alpha) [-\ln(1-\alpha)]^{\left(\frac{3}{5}\right)}$$

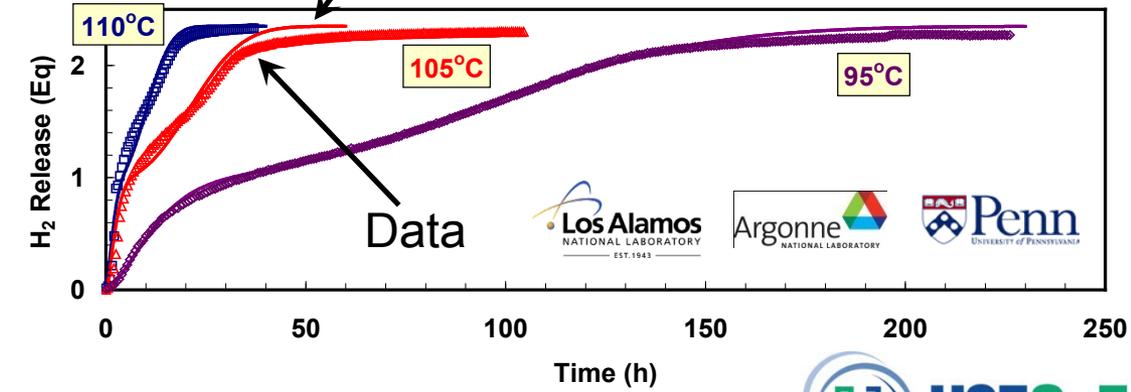
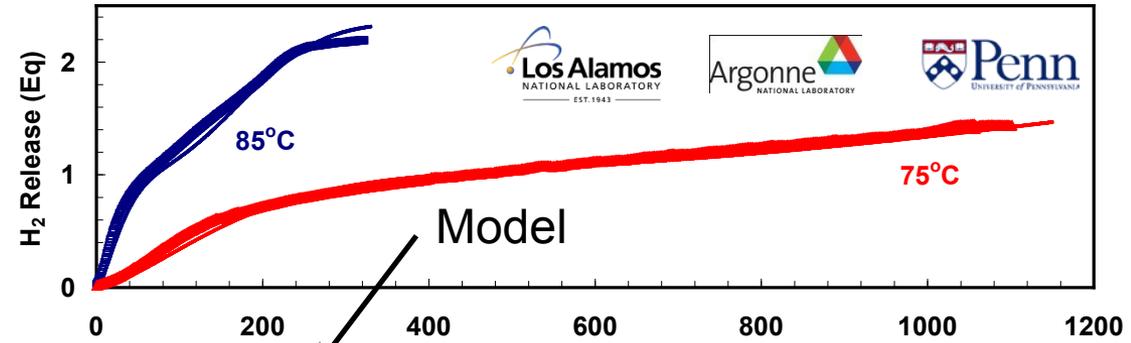


**Kinetics Used for System Modeling**

50 : 50 wt% AB : BmimCl

6.5 wt% H<sub>2</sub> (@ 2.00  $\frac{\text{mol H}_2}{\text{mol AB}}$ )

7.6 wt% H<sub>2</sub> (@ 2.35  $\frac{\text{mol H}_2}{\text{mol AB}}$ )



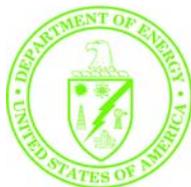
# Collaborations

External Collaborators	Effort	Contact
H <sub>2</sub> Production & Delivery Tech Team	Forecourt Requirements	S. Weil (DOE)
H <sub>2</sub> Codes and Standards	General Guidance	C. Padro (LANL)
Chemical Hydrogen Storage Researchers	Materials Updates	L. Sneddon (U. Penn)
		T. Burrell (LANL)
LANL Fuel Cell Team	Fuel Cell Impurities	T. Rockward (LANL)
		R. Borup (LANL)
H <sub>2</sub> Safety Panel	General Guidance/Concerns	S. Weiner
SSAWG	Technical Collaboration	G. Ordaz (DOE)
H <sub>2</sub> Storage Tech Team	General Guidance	Ned Stetson (DOE)
Argonne National Laboratory	Independent Analyses	R. Ahluwalia

ECoE Collaborators	Effort	Contact
UTRC	Ammonia Scrubbing	B. van Hassel
	Simulink Modeling	J. Miguel Pasini
	Safety	J. Khalil
PNNL	MOR	E. Ronnebro
	System Modeling	K. Brooks/M. Devarakonda
	BOP	K. Simmons
NREL	Vehicle Modeling	M. Thornton

# Acknowledgements

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**U.S. Department of Energy**  
**Energy Efficiency  
and Renewable Energy**

Bringing you a prosperous future where energy  
is clean, abundant, reliable, and affordable

**Fuel Cell Technologies Program: Hydrogen Storage  
Technology Development Manager: Ned Stetson**

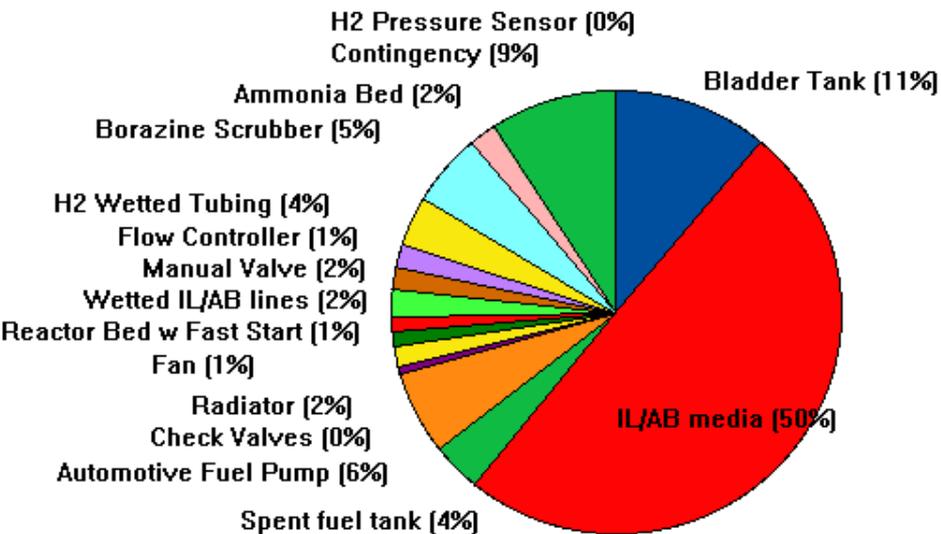
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# Backup Slides

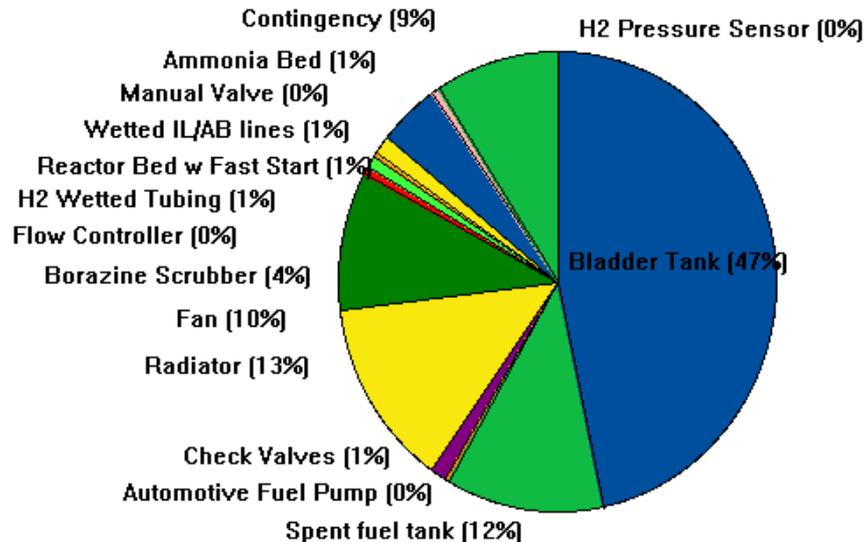
# Task 7: LANL Liquid Phase Preliminary System Design

	Calculated	System	2010 Goal	2015 Goal		Fraction of Goal
Gravimetric Density	147.85 kg	.0378	.045	.055	kg/kg	82.6%
Volumetric Density	163.3 L	.0344	.028	.040	kg/L	122%

Overall System Gravimetric BOP



Overall System Volumetric BOP



**Need to Address Gravimetric Density**

**Results are for Fluid-Phase System Shown on Slide 7**

# Task 7 Future Work: Fluid Phase System Projections

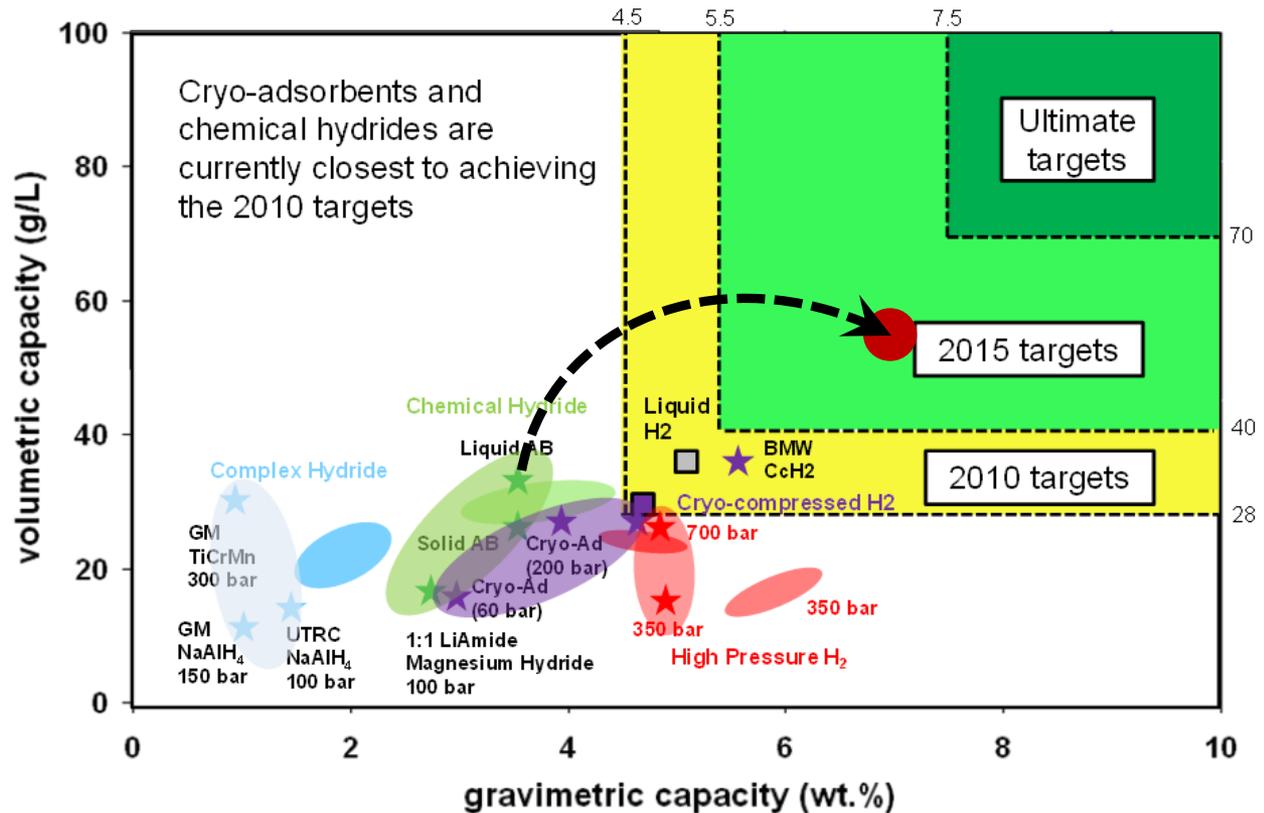
$$\text{Gravimetric Ratio} = 0.067 \frac{\text{kg } H_2}{\text{kg}_{\text{system}}}$$

$$\text{Volumetric Density} = 0.053 \frac{\text{kg } H_2}{L_{\text{system}}}$$

Assumptions:

- ½ of SS tubing
- 80 wt% solubility
- No H<sub>2</sub> purification train
- Cut 10% contingency
- 36 kW radiator
- No performance degradation
- All unit operations work as “designed”

There may be other mass and volume savings that have yet to be identified or addressed



# Task 7 Future Work: Fluid Phase System Projections

## Path A to B

- Increase solubility from 50 wt% to 80 wt% (fluid phase)

## Path A to C

- Increase from 50 wt% to 100 wt% (i.e., neat AB, upper bound)

## Path A to D

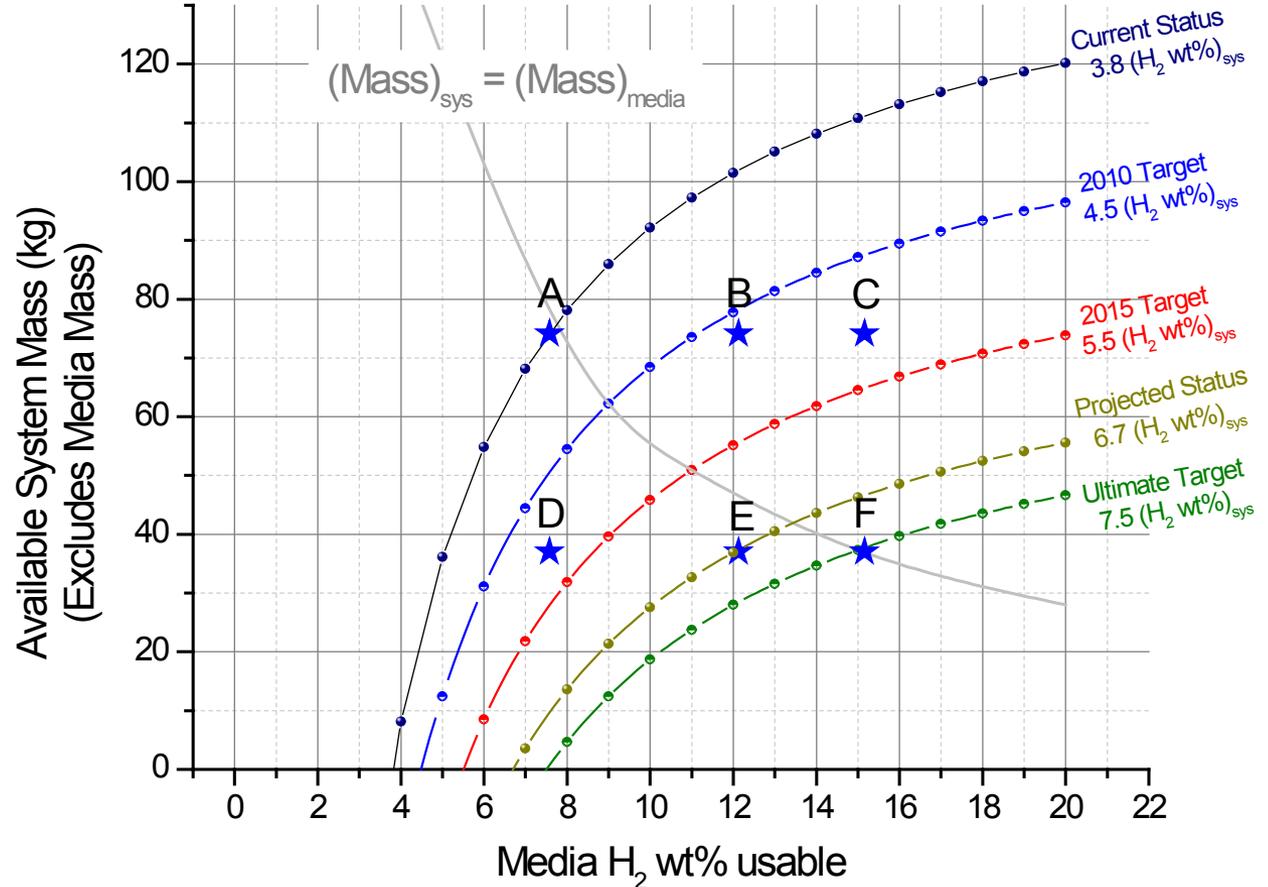
- Eliminate Mass by
  - 1/2 of SS tubing
  - No H<sub>2</sub> purification train
  - Cut 10% contingency
  - 36 kW radiator
  - No performance degradation
  - All unit operations work as "designed"

## Path A to F

- Same as A to D but increasing from 50 wt% AB to 100 wt% AB (i.e., neat AB, ultimate upper bound)

Point A = Current State-of-the-Art Fluid Phase Chemical Hydrogen Storage System

Plot of Available System Mass as a Function of H<sub>2</sub> wt% of Media  
(2.35 mol H<sub>2</sub>/mol AB) for a given System H<sub>2</sub> wt%



# Big Picture

