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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The Institute for Hydrogen and Fuel Cell Research

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_2 Discharging Rates*
    - *Start time to full flow*
    - *Transient Response*
  - *H_2 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

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The Chemical Company

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:**

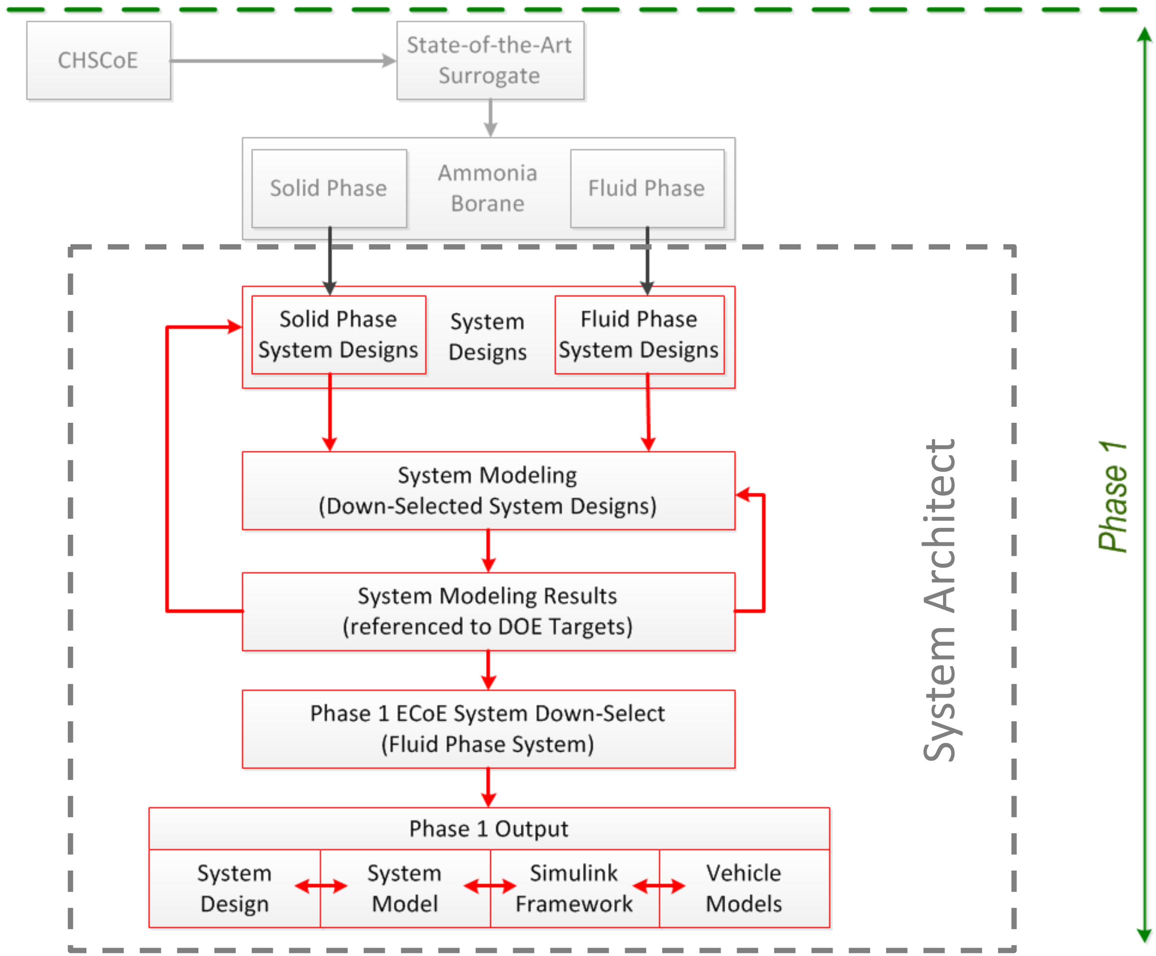
• Automotive scale fluid-phase chemical hydrogen storage system
• Ultimate Goal of the DOE
• 2015 DOE Targets Addressed: All

✓ **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



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Fluid-phase AB system down selected into Phase 2

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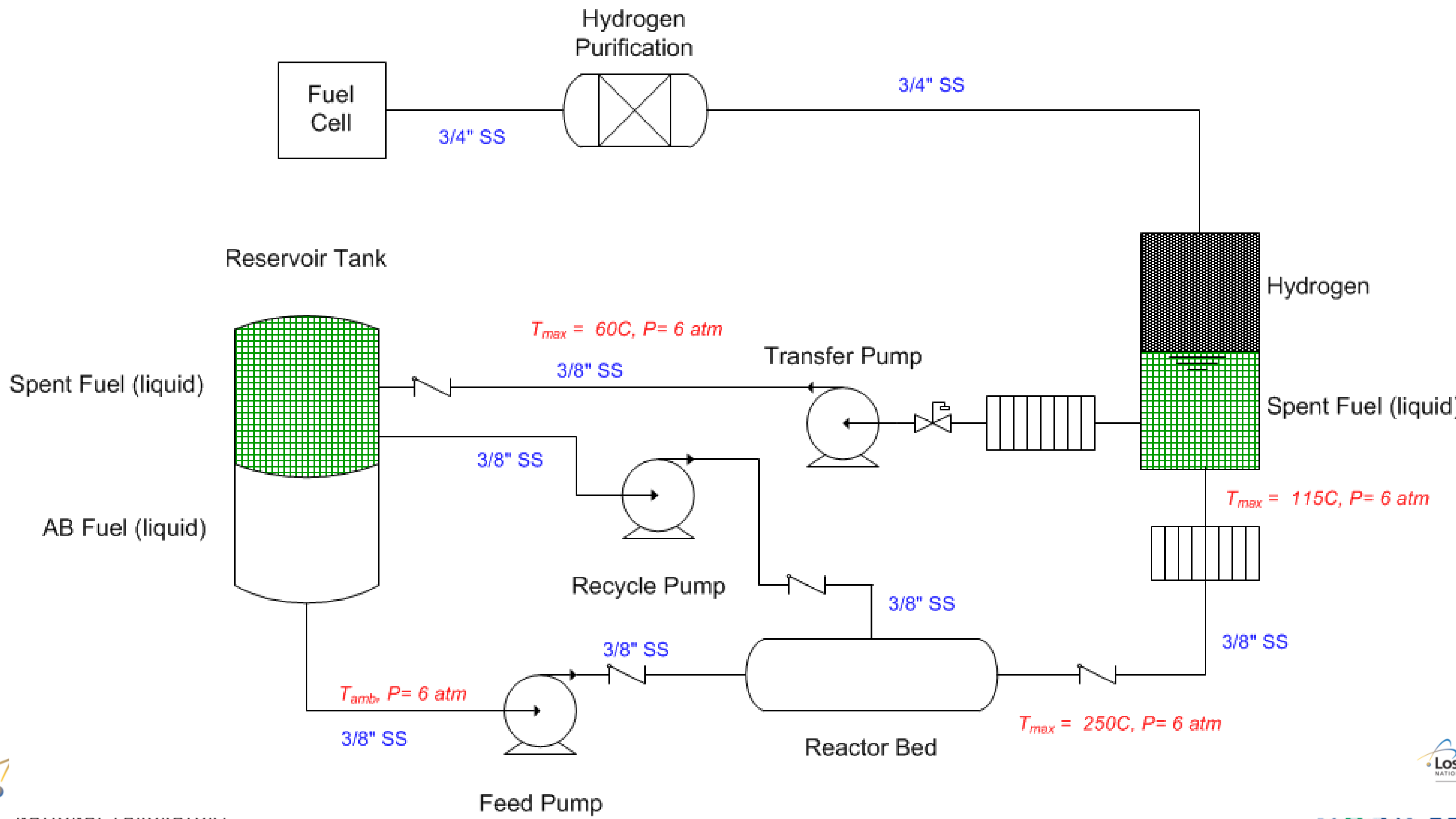
Task 7: LANL Fluid Phase System Designs

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

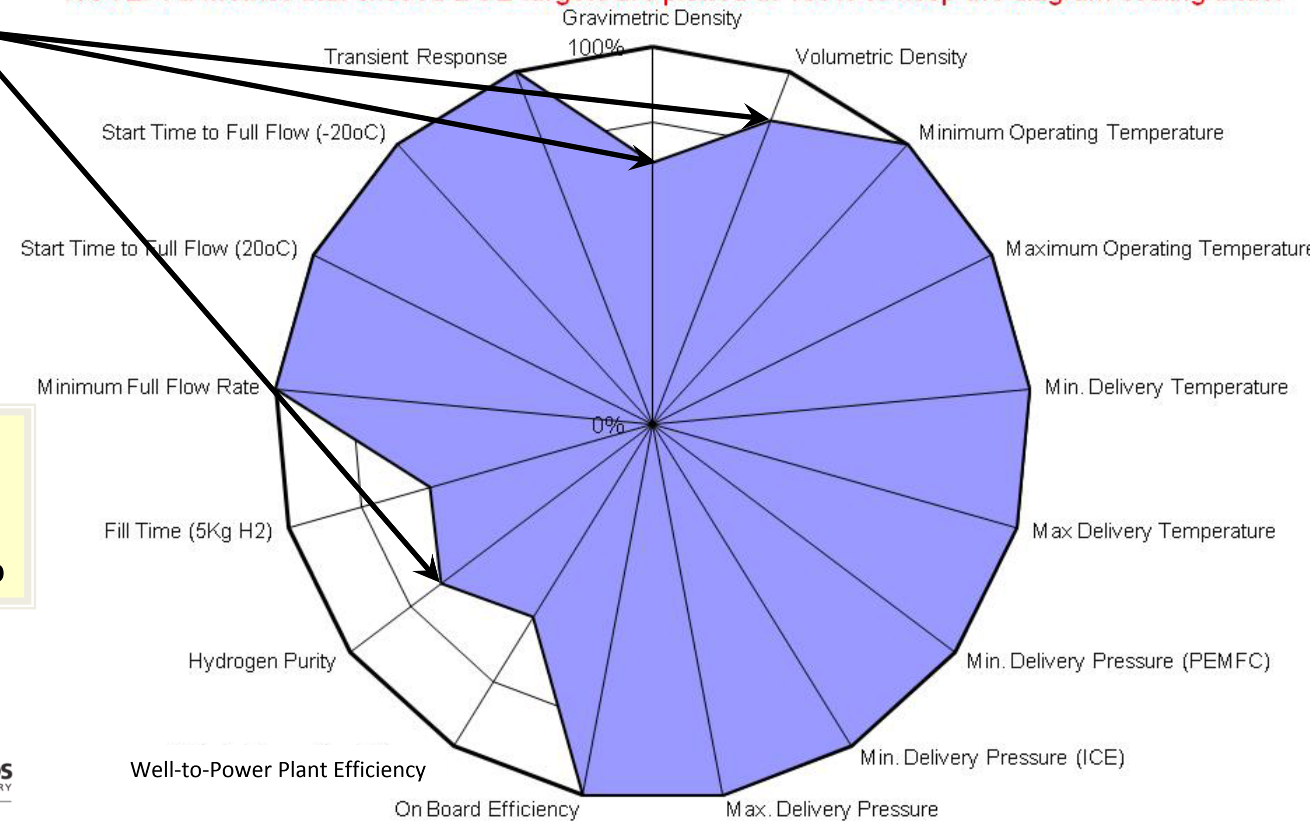
1. Gravimetric Ratio
2. Volumetric Density
3. Hydrogen Purity
4. WTPP Efficiency[a]
5. Fill Time[b]

- *[a] Not within the ECoE Research Scope*
- *[b] Target met if emptying and filling are performed simultaneously (2.7 min)*

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

DOE 2015 Targets for Liquid Ammonia Borane Flow Through System

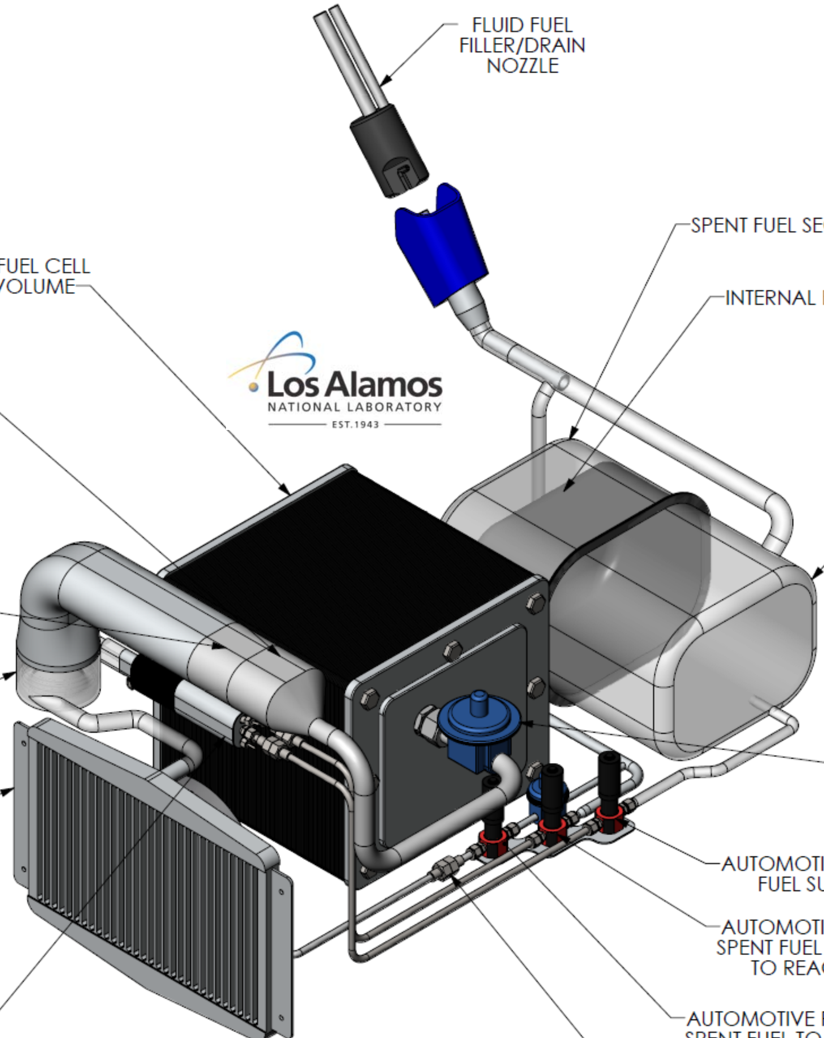
NOTE: All metrics that exceed DOE targets are plotted at 100% to keep the diagram scaling intact



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

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

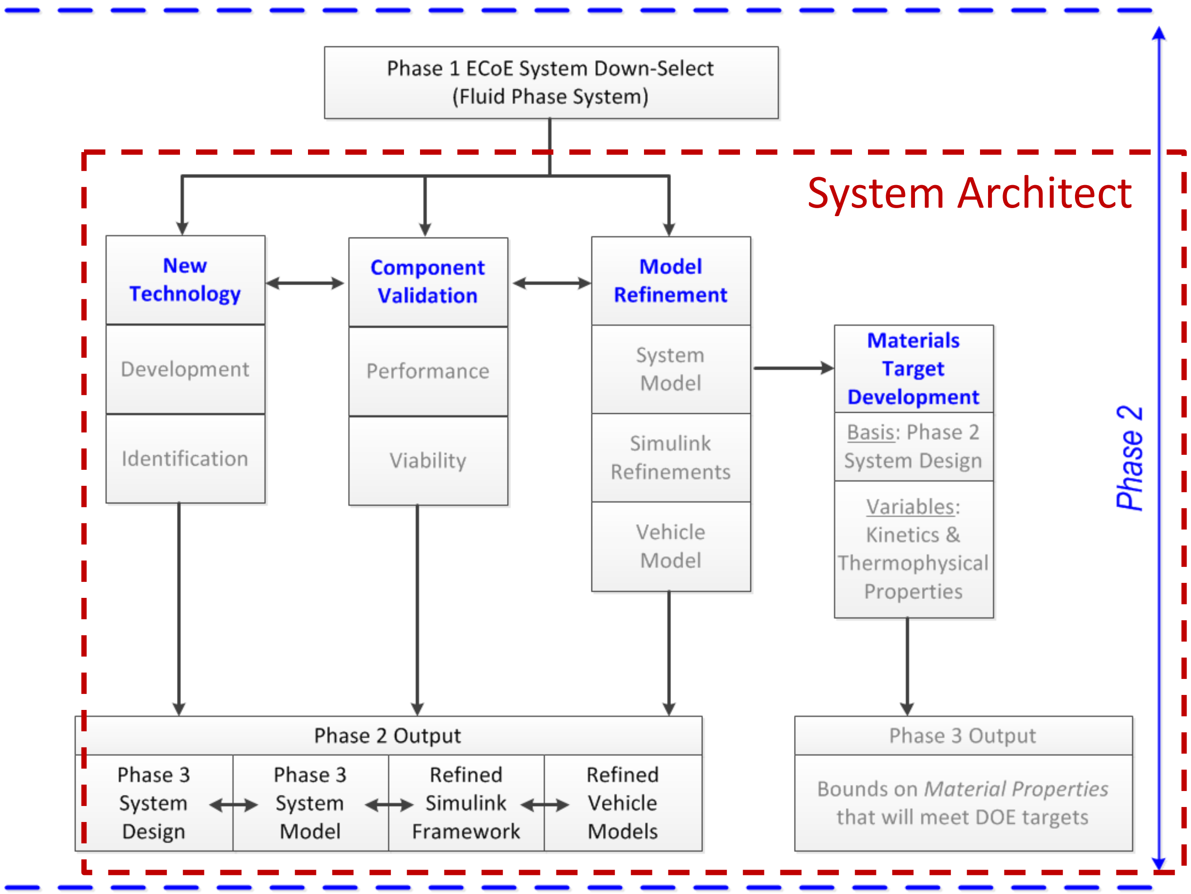
✓**Expected Outcomes:**
- Modular test bed for validating individual components or systems
- Test bed for acquiring kinetics (Task 4), impurities (Task 6), and reactor performance (Task 5)

✓**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

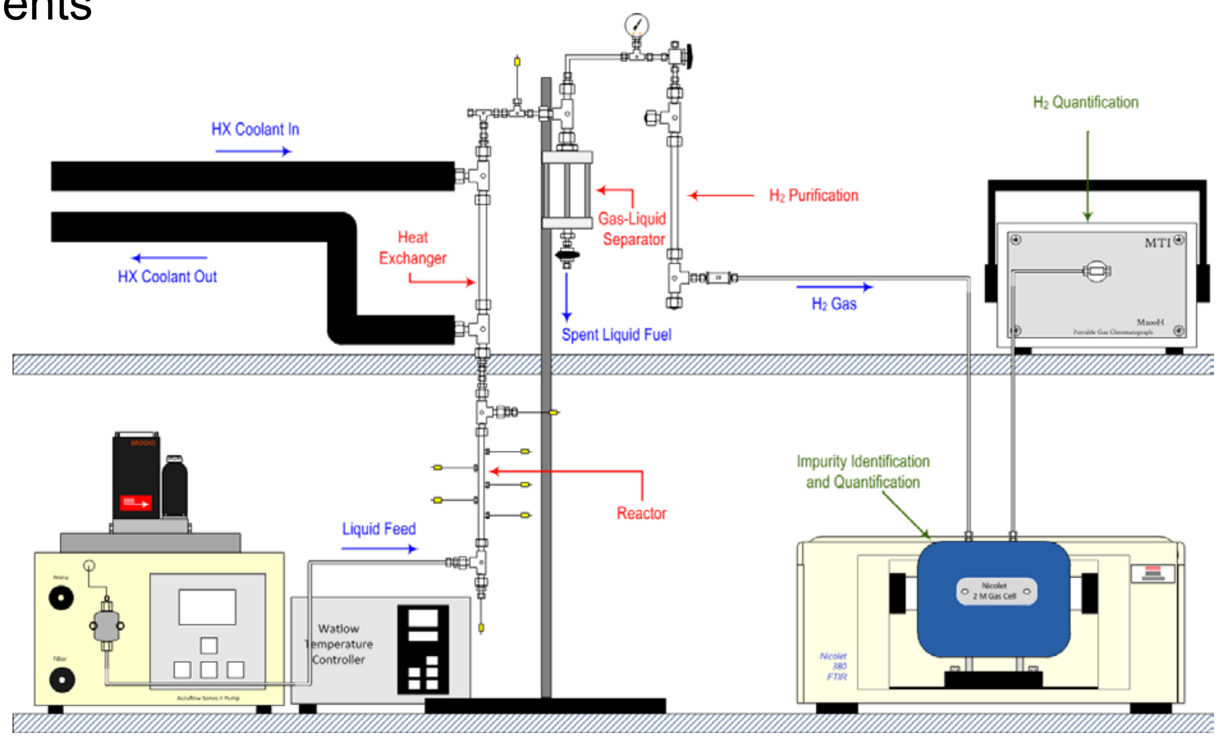


Task 7b: LANL Fluid-Phase Validation Test Bed

- **Fluid Phase System Component Validation Setup**

➢ <u>Deployed for Phase 2 Activities</u>

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

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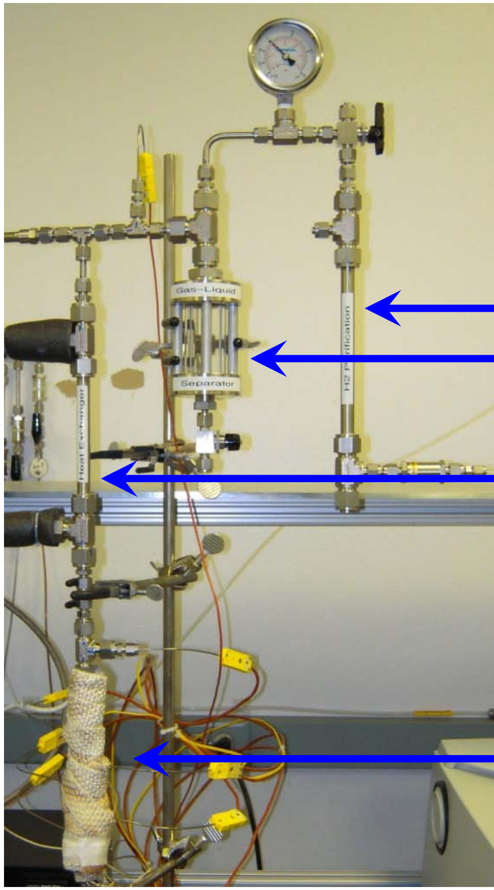
Task 7b: LANL Fluid-Phase Validation Test Bed

- **Fluid Phase Chemical Hydride System Component Validation Setup**

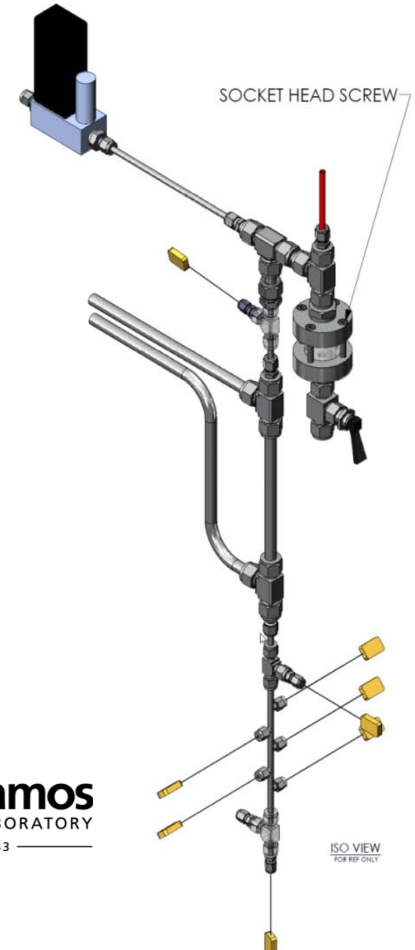


H_2 Purification

Gas-Liquid Separator

Heat Exchanger

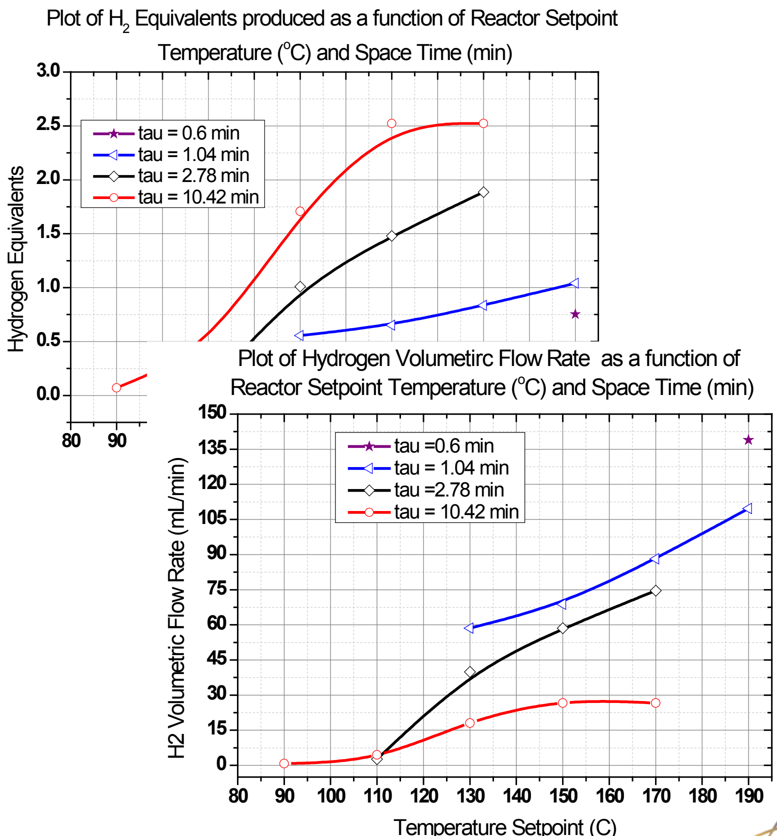
Reactor



Modular Design Allows for Validating Individual System Components or Integrated Systems

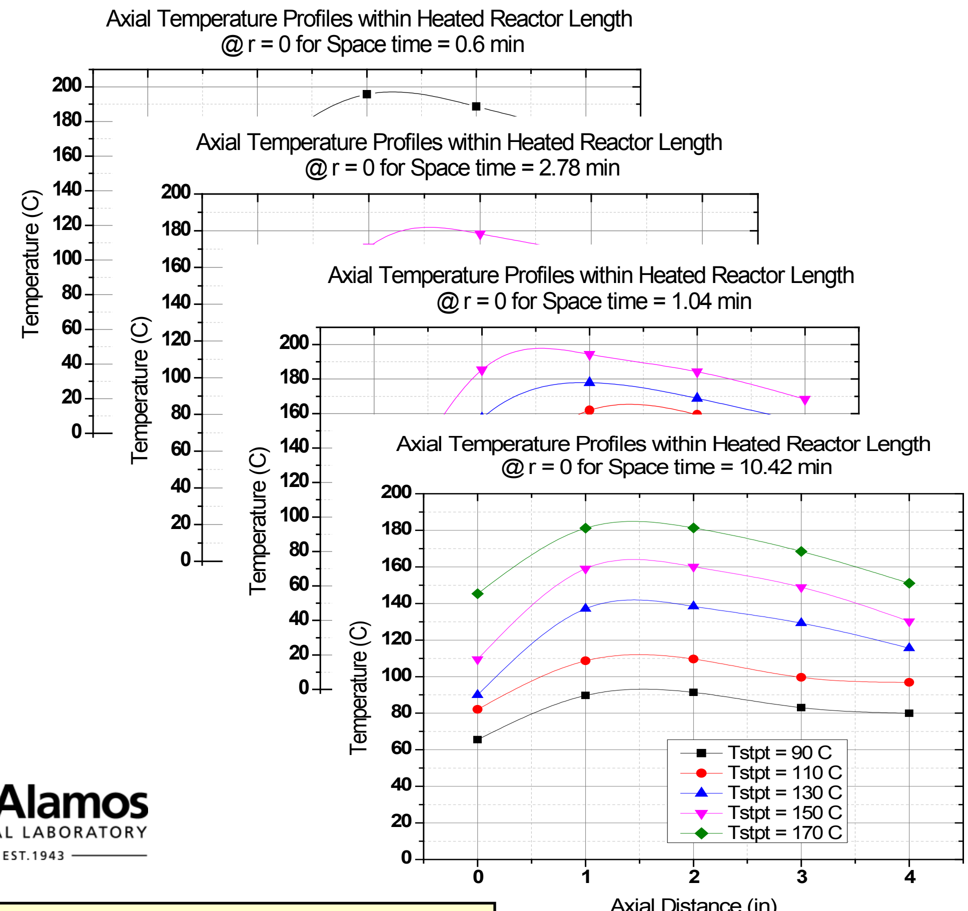
Task 7b: LANL Fluid-Phase Validation Test Bed

- **Kinetics Results from Using Fluid Phase AB as a H_2 Source**



Zeolite Scrubber used for H_2 Purification

- **Axial Temperature Profiles Observed from Using Fluid Phase AB as a H_2 Source**



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Fluid-Phase Reactor Test Bed Validated

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Task 7b Summary and Future Work: Test Bed

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 *(DEMONSTRATED)*	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 *(Go)*	+/- 5% of H_2 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*

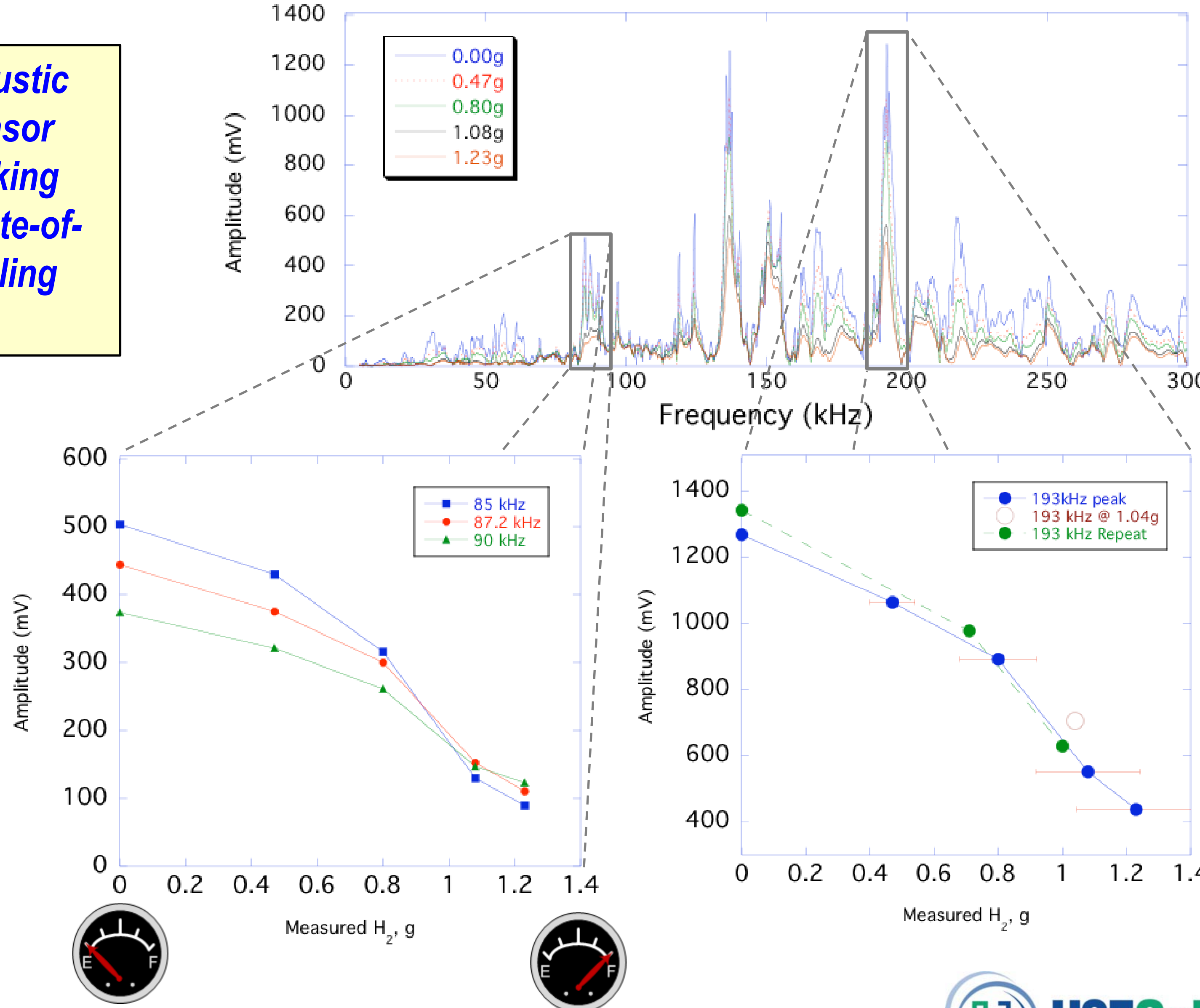
❖ **Milestone**

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



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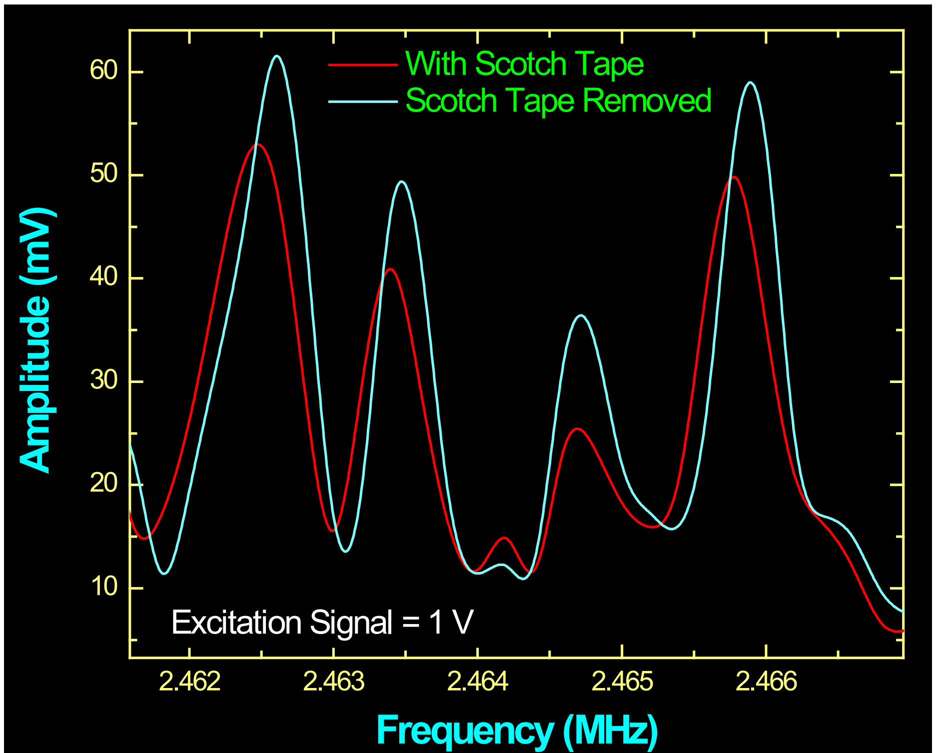
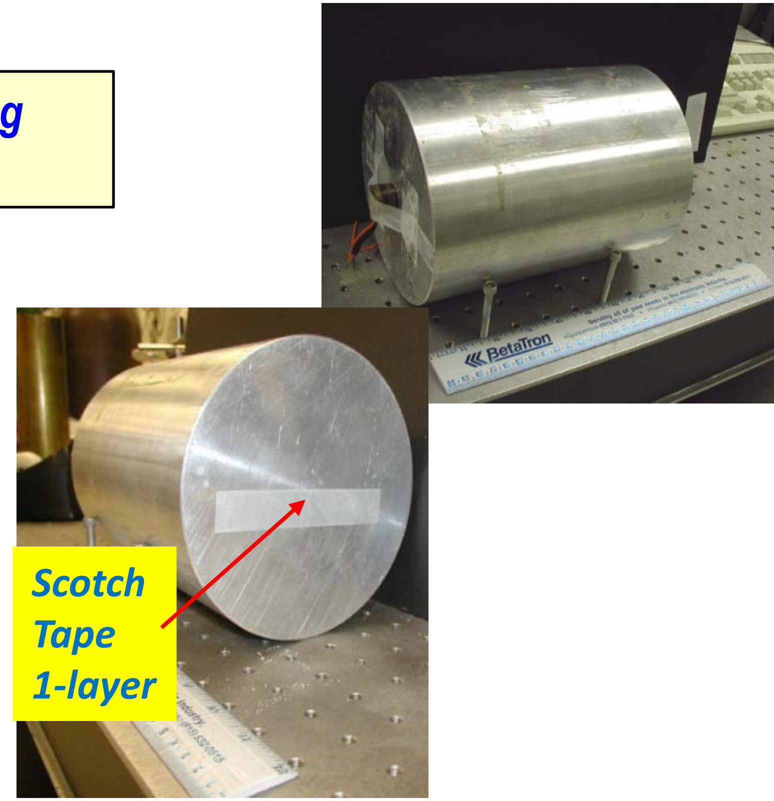
Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

LANL Acoustic Sensor Capable of Monitoring Containment Vessel Integrity





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Task 2 Summary & Future Work: Fuel Gauge Sensor

Summary

- Demonstrated acoustic fuel gauge sensor proof-of-principle on various metal hdyrides
- 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_2 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_2 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

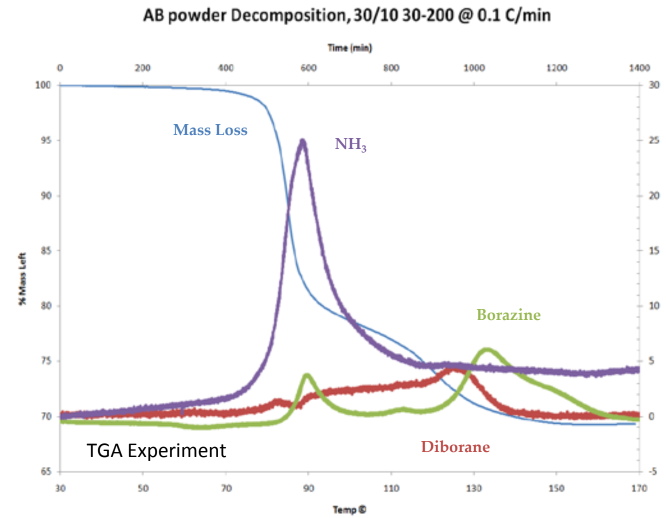
❖ Go/No-Go

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

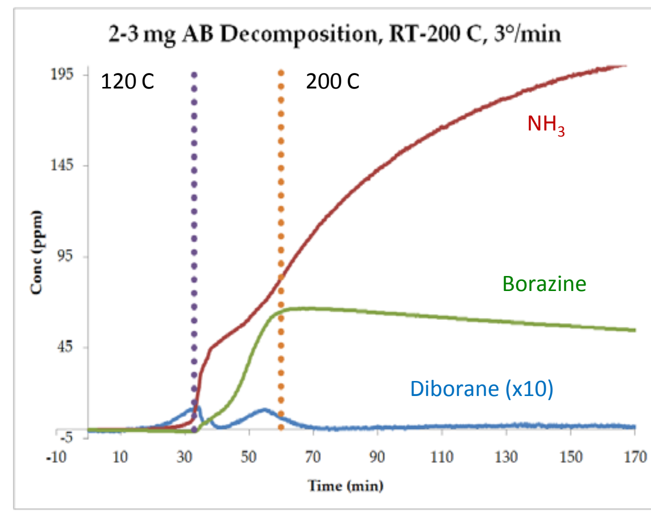
Material	Onset T (°C)	Wt % (SD)		
		NH_3	Borazine	Diborane
AB	95	2.5 0.71	3.8 0.71	1.8 0.35
Powder AB	82	2.7 0.42	2.2 0.21	0.99 0.0077
AB/MC	77	4.6 1.0	2.0 0.35	0.85 0.071

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



Adsorption Media Tested

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



Batch Reactor Experiment

✓ ***Impurities can be scrubbed via adsorption media***

but…….

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

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Task 6: Hydrogen Impurities and Mitigation

- **Fuel Cell Tolerance Test with Diborane**

VI-Curve:

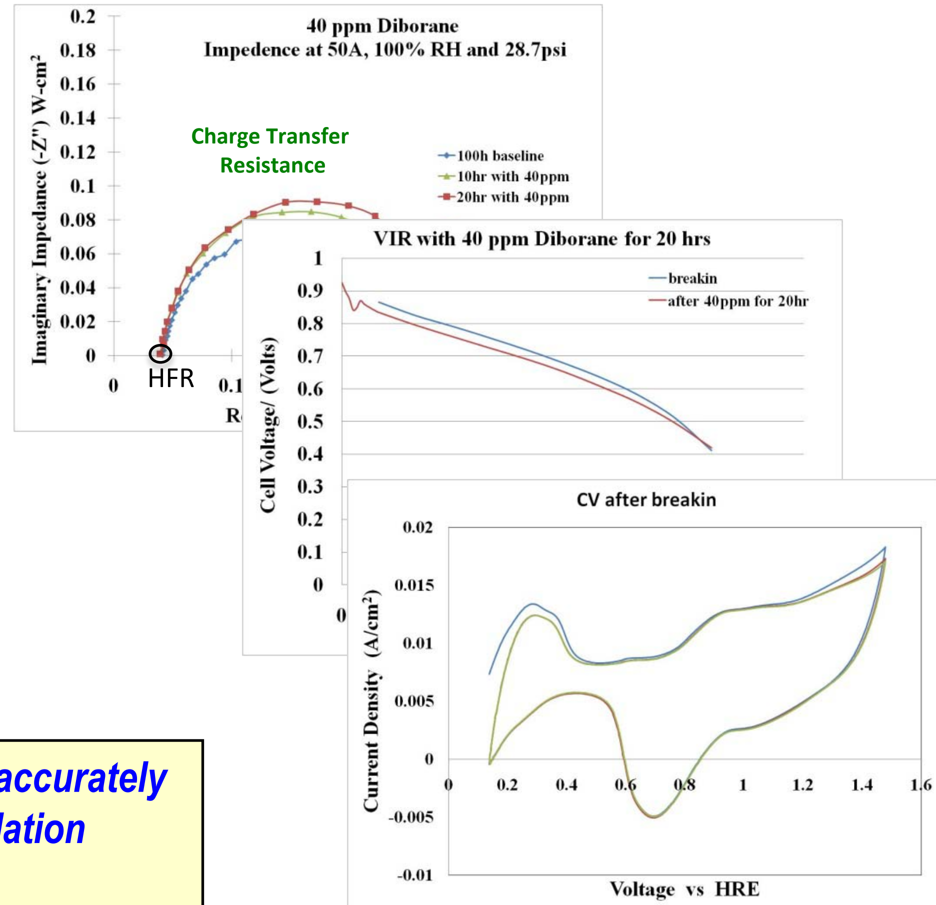
- Losses (~20mV) were observed after 20h of exposure

AC Impedance:

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

Cyclic Voltammetry:

- No effect on catalyst surface area



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

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

Preliminary Test Indicate Diborane Affects the Charge Transfer Resistance

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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

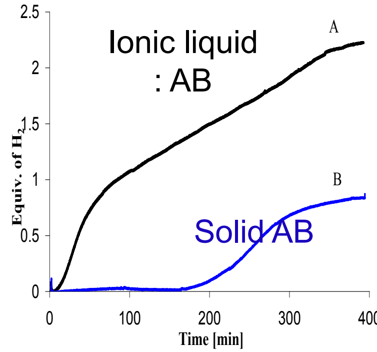
- Quantify impurities using fluid-phase bench-scale validation test bed **(*TASK 7b*)**
- Examine impurity mitigation strategies (i.e., catalysts, temperature control, conversion, space-time, etc.) on reaction selectivity

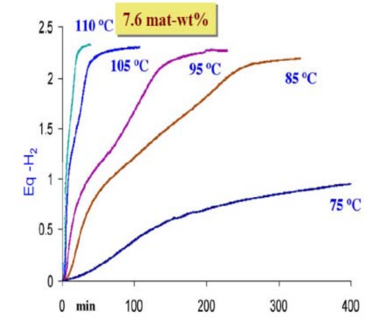
Task 4: Reaction Rate Models for AB/IL Systems

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

$$\left(r_{H_2}\right)\Big|_{0.00}^{1.00} = 1.5\left[\left(2.26056\times10^{17}\right)e^{\frac{-142\,kJ/mol}{RT}}\right]\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{\left(\frac{1}{3}\right)}$$

$$\left(r_{H_2}\right)\Big|_{1.00}^{2.35} = 2.5\left[\left(1.09026\times10^{17}\right)e^{\frac{-146\,kJ/mol}{RT}}\right]\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{\left(\frac{3}{5}\right)}$$



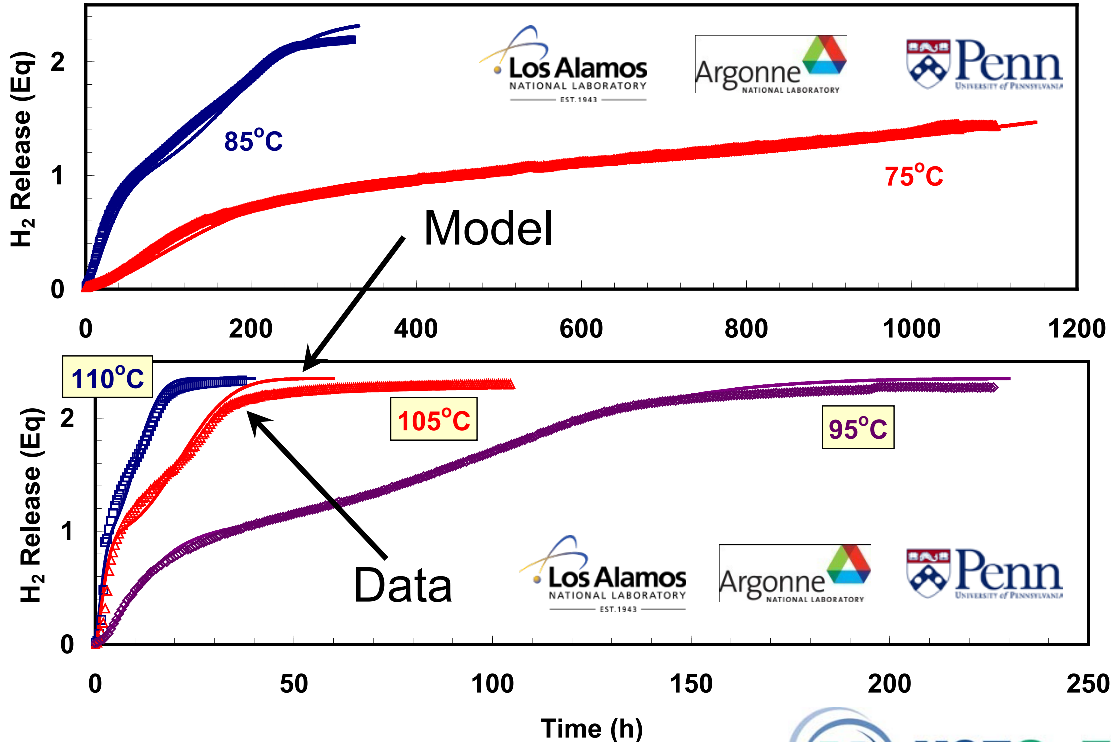


Kinetics Used for System Modeling

$$\underline{50:50\ wt\%\ AB:BmimCl}$$

$$6.5\ wt\%\ H_2\left(@\ 2.00\frac{mol\ H_2}{mol\ AB}\right)$$

$$7.6\ wt\%\ H_2\left(@\ 2.35\frac{mol\ H_2}{mol\ AB}\right)$$



Collaborations

External Collaborators	Effort	Contact
H_2 Production & Delivery Tech Team	Forecourt Requirements	S. Weil (DOE)
H_2 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_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

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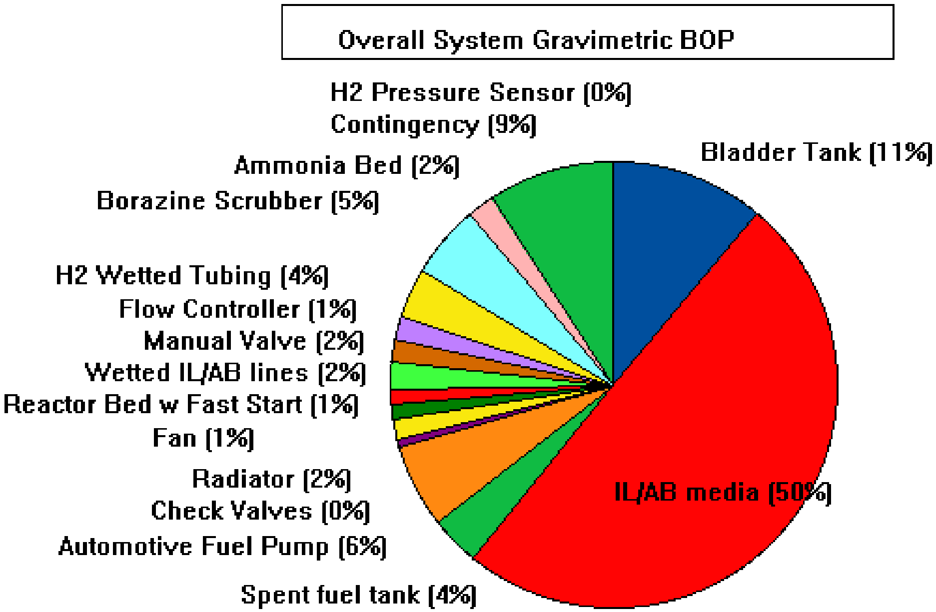
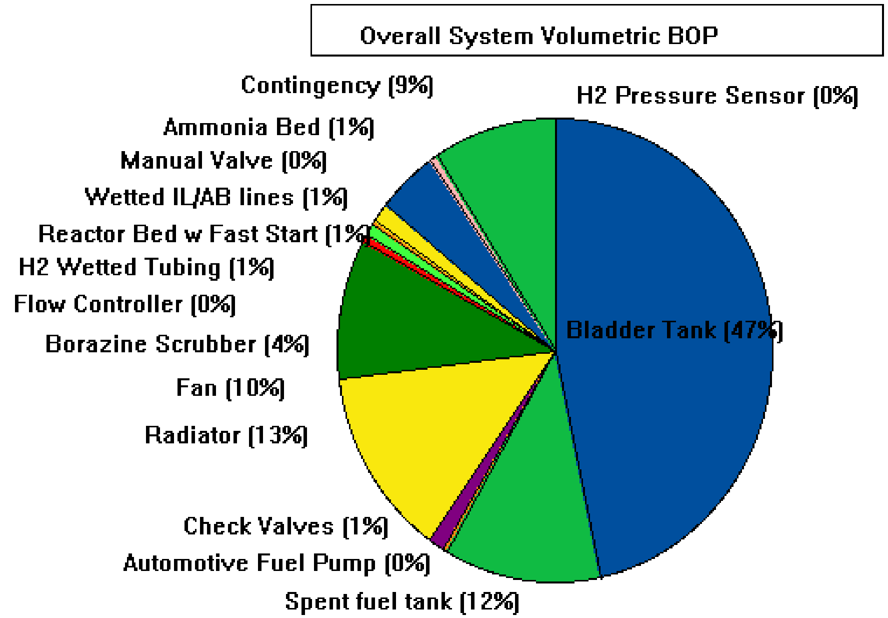
Fuel Cell Technologies Program: Hydrogen Storage
Technology Development Manager: Ned Stetson

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%





Need to Address Gravimetric Density

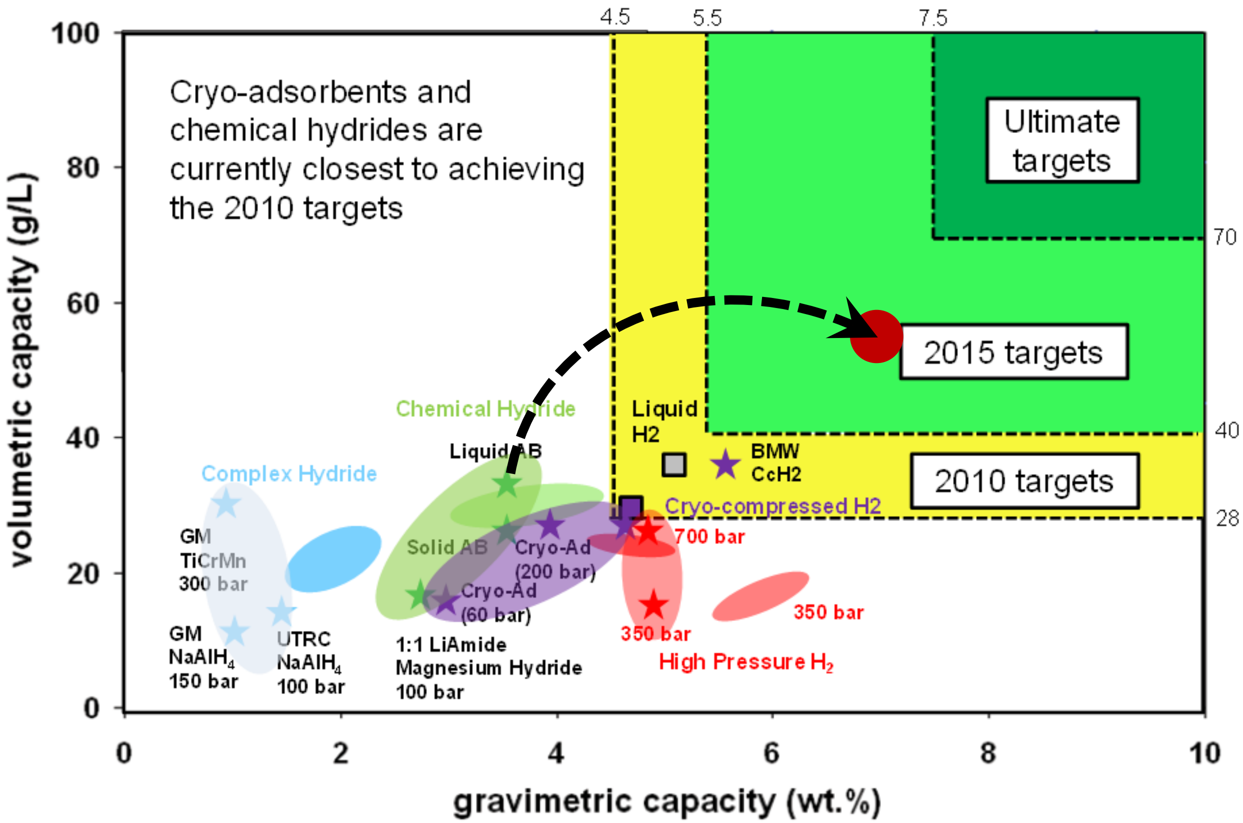
Results are for Fluid-Phase System Shown on Slide 7

Task 7 Future Work: Fluid Phase System Projections

$$Gravimetric\ Ratio = 0.067 \frac{kg\ H_2}{kg_{system}} \qquad Volumetric\ Density = 0.053 \frac{kg\ H_2}{L_{system}}$$

Assumptions:

- ½ of SS tubing
- 80 wt% solubility
- No H_2 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

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Task 7 Future Work: Fluid Phase System Projections

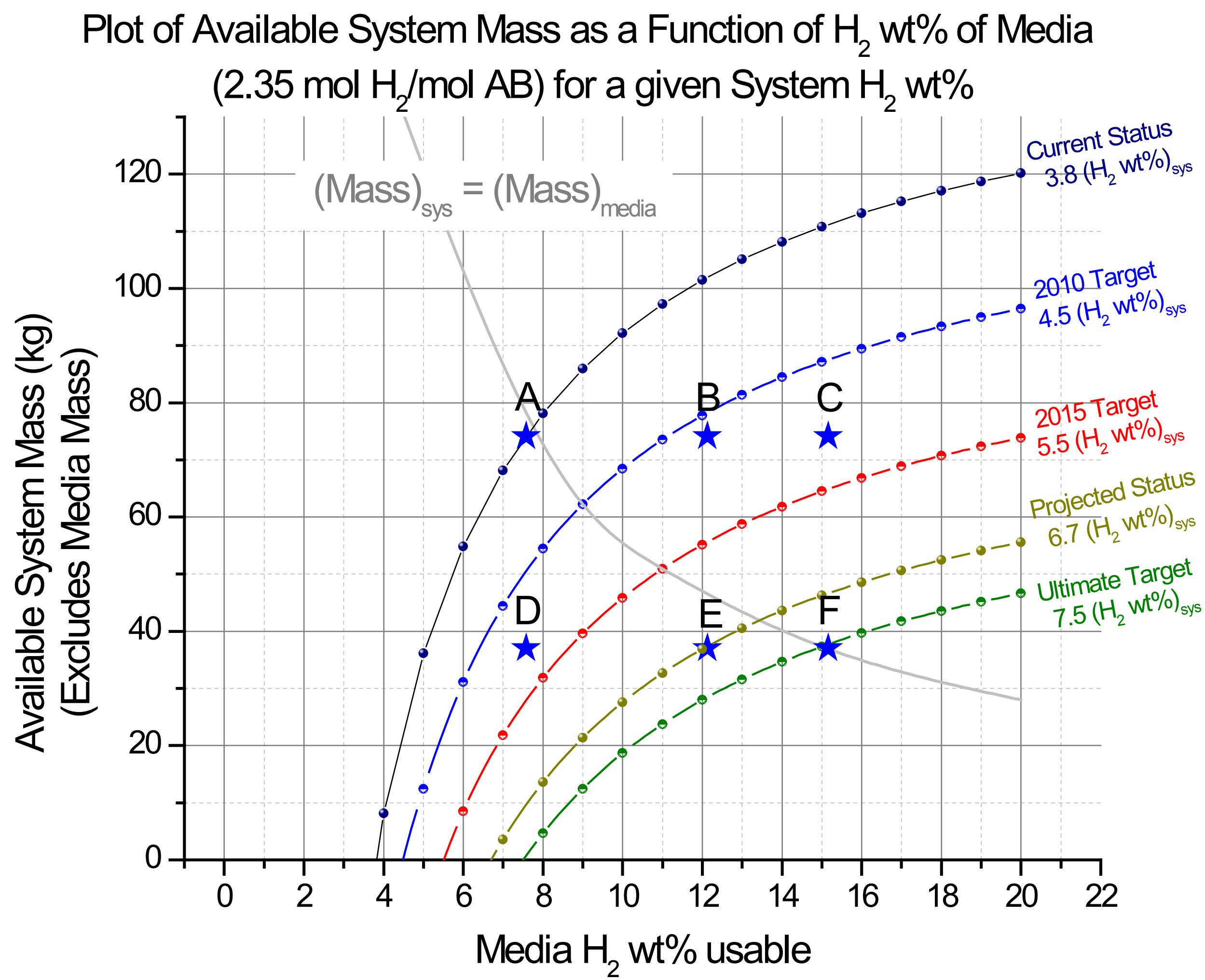
Path A to B
- Increase solubility from 50 wt% to 80 wt% (fluid phase)

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

Path A to D
- Eliminate Mass by
  - ½ of SS tubing
  - No H_2 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



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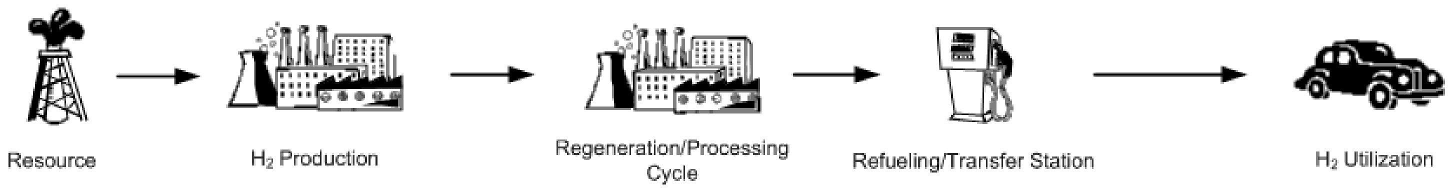
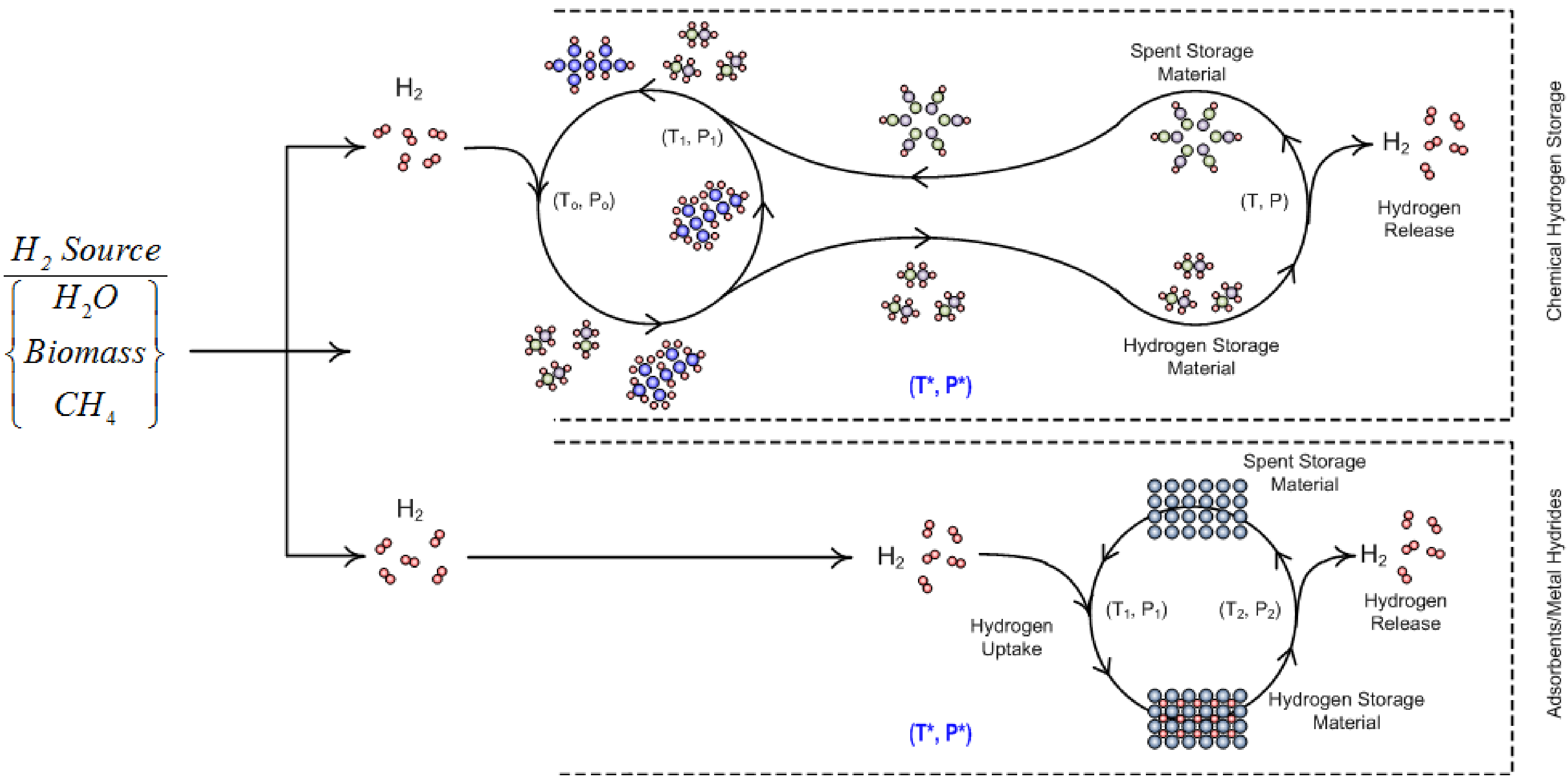
Big Picture


Resource
H_2 Production
Regeneration/Processing Cycle
Refueling/Transfer Station
H_2 Utilization


H_2 Source
H_2O
Biomass
CH_4
H_2
(T_1, P_1)
(T_0, P_0)
Spent Storage Material
(T, P)
H_2
Hydrogen Release
Hydrogen Storage Material
(T*, P*)
Chemical Hydrogen Storage
H_2
H_2
Spent Storage Material
H_2
Hydrogen Uptake
(T_1, P_1)
(T_2, P_2)
Hydrogen Release
Hydrogen Storage Material
(T*, P*)
Adsorbents/Metal Hydrides