Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

D. Herling, **K. Brooks, E. Ronnebro, S. Rassat, K. Simmons, M. Weimar**

DOE Fuel Cell Technology Program
Annual Merit Review

June 8, 2010
Technology Development Manager: Monterey Gardiner

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

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Project ID: ST005

Overview

- Timeline
  - Start: Feb. 2009
  - Project End: Jan. 2014
    - End Phase 1: 2011
    - End Phase 2: 2013
    - End Phase 3: 2014
- Budget
  - $6.2M Total (PNNL) anticipated
    - DOE direct funded
    - No cost-share required for National Lab
  - FY09: $600k
  - FY10: $1.5M
- Barriers
  - A. System Weight and Volume
  - B. System Cost
  - C. Efficiency
  - D. Durability
  - E. Charging/Discharging Rates
  - G. Materials of Construction
  - H. Balance of Plant (BOP) Components
  - J. Thermal Management
  - O. Hydrogen Boil-Off
  - S. By-Product/Spent Material Removal
- Partners

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Introduction: PNNL Scope in HSECoE

- Roles Supporting Engineering Center Structure
  - Technology Area Lead (TAL) for Materials Operating Requirements
  - Coordinate activities as the Technology Team Lead (TTL)
    - Bulk Materials Handling (Transport Phenomena)
    - Pressure Vessels (Enabling Technologies)
    - Manufacturing and Cost Analysis (Performance Analysis)
  - Liaison to VT Program projects and resources
- Technology Development and System Engineering Tasks
  - Solid Chemical Hydride System Design
  - Process Modeling & Engineering
  - Kinetics & Materials Characterization
  - Microarchitectures Device Development
  - Materials Reactivity & Compatibility
  - Containment and Pressure Vessel Design
  - Manufacturing & Cost Analysis

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Relevance: Hydrogen Storage

- Impact to FCT Program
  - Demonstrate high level of performance that meets DOE 2015 targets using solid chemical hydrogen storage
  - Apply materials discoveries and knowledge developed as part of the Materials Centers of Excellence
- Hydrogen Storage Community at Large
  - Develop and/or advanced modeling and simulation tools for the optimum design and engineering of on-board storage systems
  - Functional prototype systems available to OEMs
  - Engineering methodologies, analysis tools, and designs applicable to stationary storage and portable power applications
  - U.S. demonstration of on-board storage to advance state of the art globally

Approach: Objectives and Deliverables

- Technical Objectives of PNNL Scope
  - Design of chemical hydride hydrogen storage system & balance of plant (BoP) components
  - Reduce system volume and weight and optimize storage capability, fueling, and hydrogen supply performance
  - Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability
  - Demonstrate the performance of economical, compact, lightweight vessels for hybridized storage
  - Guide design and technology down selection through cost modeling and manufacturing analysis
- Program and annual Deliverables established
- Phased/gated progressions aligning with HSECoE go/no-go decisions

Focus is on Process Engineering, System Design and Functional Integration

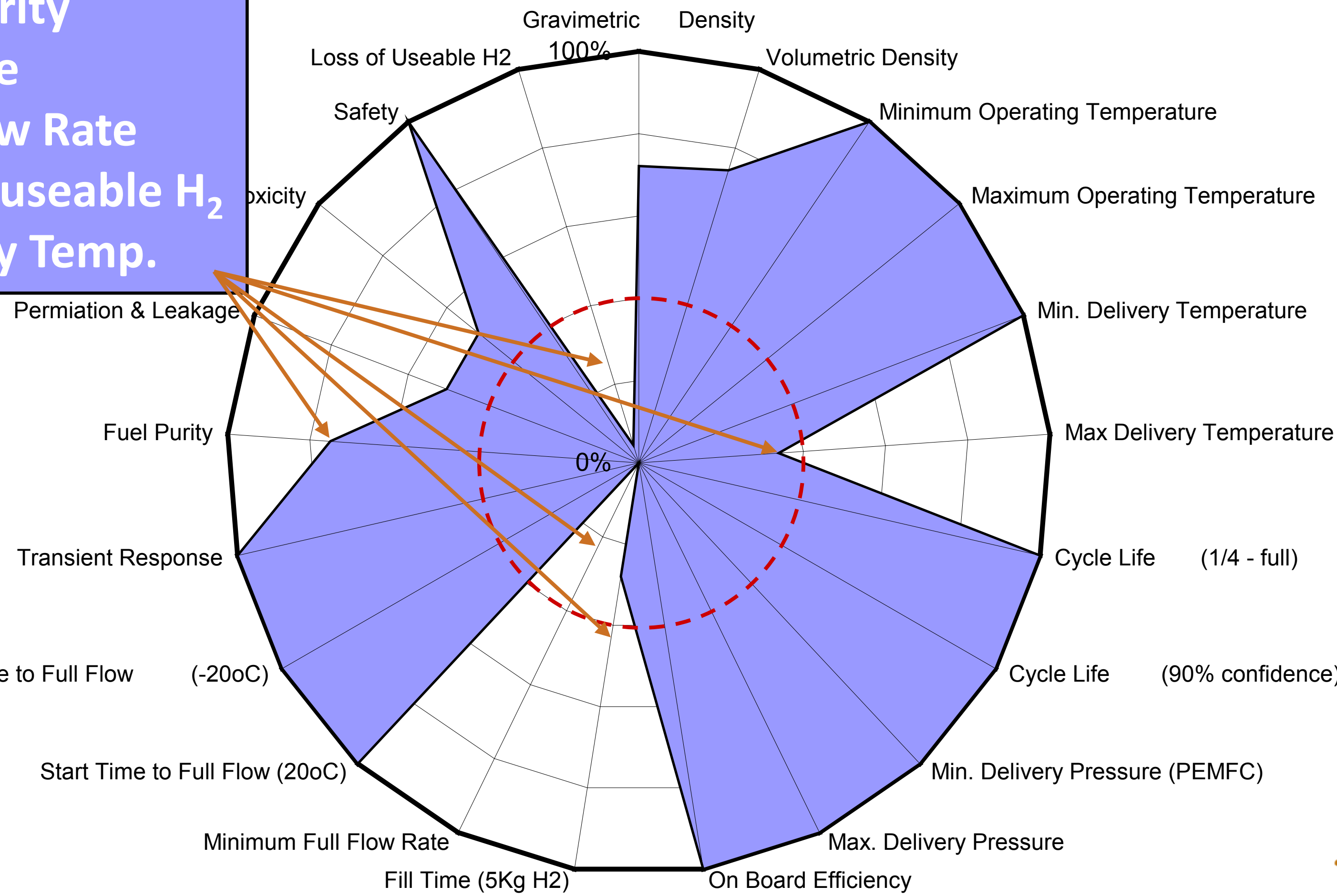
Accomplishment: Milestones FY10

Q1	Task 7	**Provide Rev.0 cost model, structure details and spreadsheet to Center partners for their evaluation.**
Q2	Task 1	**Complete preliminary design for fuel element transfer system (solids handling coupled to reactor).**
Q2	Task 2	**Complete COMSOL modeling of configurations**
Q2	Task 2	**Down select systems to be modeled for transient response**
Q3	Task 3	**Complete test station for monolithic fuel element and hydrogen release measurement**
Q3	Task 1	**Determine functional criteria and design rules based on modeling performance predictions and hydride system needs.**
Q3	Task 2	**Complete a conceptual design for a solid chemical hydride reactor that will provide input to the HSECoE’s Phase 1 Go/No-go decision making process, and insight into the ability of such a system to meet the 2015 volumetric capacity target of 1.5 kWh/L.**
Q3	Task 3	**Determine bulk kinetics measurements and impact on performance.**
Q3	Task 6	**Complete modeling and establish pressure vessel design rules for use with prototypes.**
Q4	Task 4	**Complete assessment on the probability of integrating a heat exchanger within storage vessel.**
Q4	Task 5	**Complete identification of known materials compatibility issues and establish corrective action plan for component designs.**

Chemical Hydride System Status
Solid Ammonia-Borane: 2010 Targets

- 17 Targets Above 40%
- 4 Targets Undetermined or Below 40% Minimum

1. Fuel Purity
2. Fill Time
3. Full Flow Rate
4. Loss of useable H_2
5. Delivery Temp.



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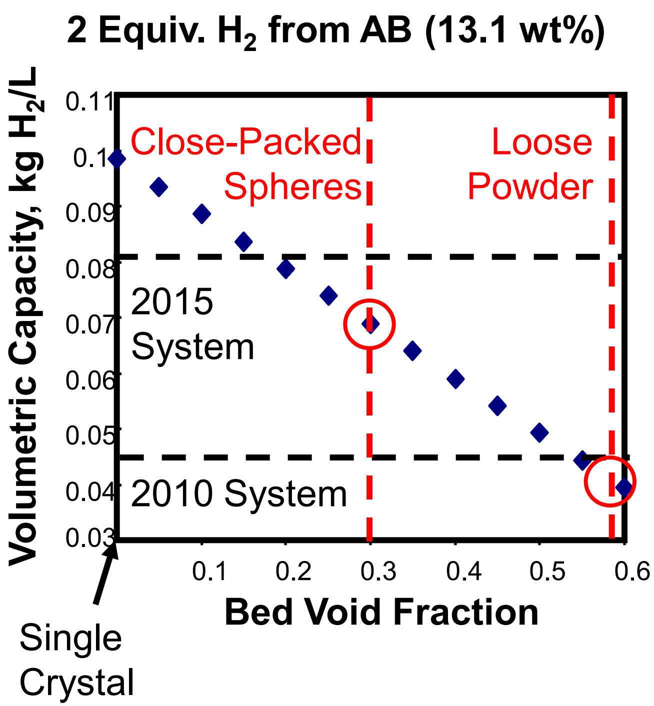
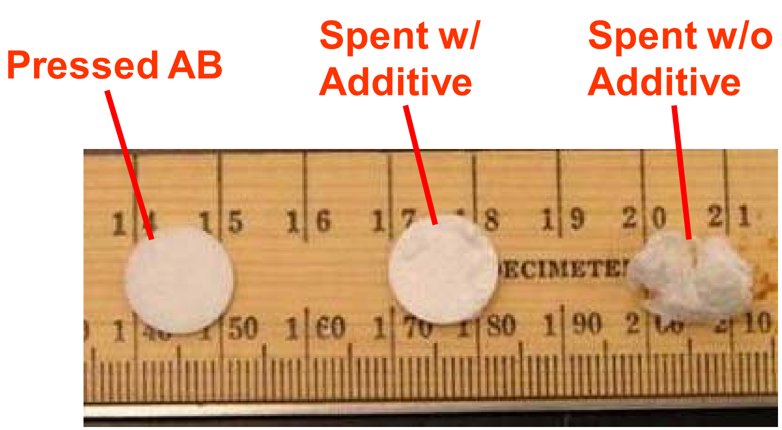
Source: Anton 2010 HSECoE program AMR

Primary Engineering Barriers for Chemical Hydride Systems

- Chemical Hydrides are not 'reacted' in the fuel tank
  - Solids handling engineering key part of any system concept
  - Exothermic reaction of most systems requires different thermal management solutions compared to MH or absorbents
  - AB thermolysis at <100°C; long term storage in hot climates?
- DOE Technical Targets:
  - BoP components and will add to
  - Performance impact of impurities needs a solution
  - Loss of Useable Hydrogen (g/hr)/kg H2 stored: 0.1 (2010) & 0.05 (2015); loss includes venting, if required
- Re-fueling vehicle logistics can be a challenge
- Ammonia Borane foams on reaction – potential limitation to practical engineering application

Engineered Form-Factor for Solid AB





- System targets are difficult for granulated materials
- AB foams when it releases hydrogen – not conducive to engineering
- Antifoaming approaches key
  - More than 50 additive formulations tested with 2-3 successful (CHCoE study)
  - Scaffold materials also demonstrate foam suppression at lower AB:scaffold loadings
  - Paves way for system with monolithic fuel & high volumetric density

Additive suppresses foaming and enables monolithic fuels

Source: PNNL CHCoE

Integrated System Design and Process Modeling for Solid Ammonia Borane

System Modeling Approach

- Ballast Tank
  - Provides H2 for start-up and transients
- No Heat Addition
  - Exothermic reaction heat warms incoming AB
- Issues/Assumptions
  - High heat transfer required between oil and AB in augers (heat/cool)
  - Extrapolation of kinetic data at 160°C to > 500°C
  - Modeling counterflow in Simulink
  - High Pressures in Ballast Tank—need for carbon fiber tank
  - No reaction in heated auger
  - Sticky AB during phase change
  - Impurity Borazine

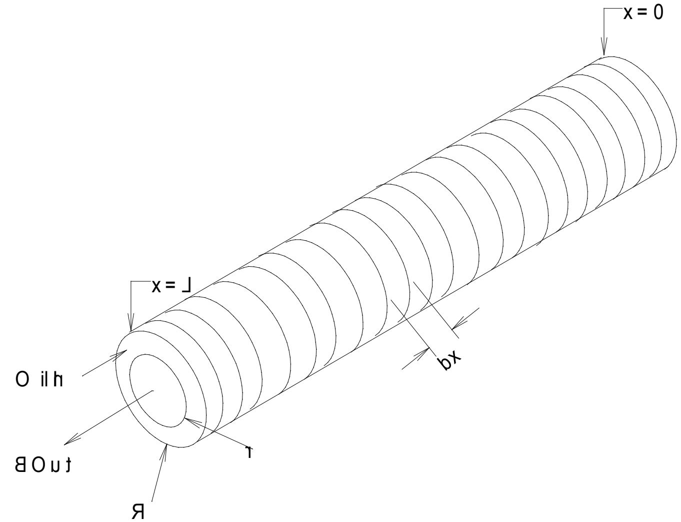
BoP Equipment Equations/Assumptions

- Heated Auger
  - Psuedo Counterflow (co-flow section configured in counterflow)
  - Transient (includes metal thermal mass)
  - Assumes HT Oil → Metal → AB, No axial conduction
- Cooled Auger
  - Counterflow Heat Exchanger
  - Steady State (NTU-Effectiveness Method)
- Burner
  - Co-Flow
  - Transient (includes metal thermal mass)
  - Assumes HT Gas → Metal → Oil, No axial conduction
- Radiator
  - Cross Flow Heat Exchanger

Example Simulink Component Modeling

Oil Energy Equation

$$\pi\left(R_{in}^{\;2}-r_{out}^{\;2}\right)\rho_{oil}C_{p,oil}\left(\frac{\partial T_{oil}}{\partial t}+u_{oil}\frac{\partial T_{oil}}{\partial x}\right)+2\pi r_{out}h_{oil-metal}\left(T_{oil}-T_{metal}\right)=0$$



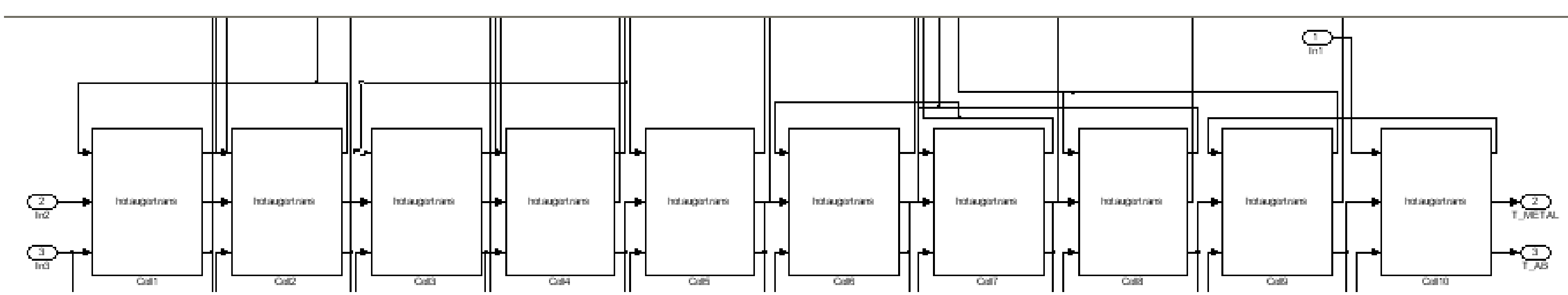
Metal Energy Equation

$$\pi\left(r_{out}^{\;2}-r_{in}^{\;2}+r_{auger}^{\;2}\right)\rho_{metal}C_{p,metal}\left(\frac{\partial T_{metal}}{\partial t}\right)+2\pi r_{out}h_{oil-metal}\left(T_{metal}-T_{oil}\right)$$

$$+2\pi(r_{in}+r_{auger})\varphi h_{metal-AB}\left(T_{metal}-T_{AB}\right)=0$$

AB Energy Equation

$$\pi r_{in}^{\;2}\rho_{bulk,AB}C_{p,AB}\left(\frac{\partial T_{AB}}{\partial t}+u_{AB}\frac{\partial T_{AB}}{\partial x}\right)+2\pi r_{in}\varphi h_{metal-AB}\left(T_{AB}-T_{metal}\right)=0$$



Integrated System Simulation

- Components in the model are coded as ‘C’ s-functions and simulated in Matlab/Simulink
- Control scheme is based on fuel cell demand and ballast tank states
- Start-Up assumed with 60 kWe power requirement
- Drive Cycle assumed after start-up

Integrated System Simulation

- Components in the model are coded as 'C' s-functions
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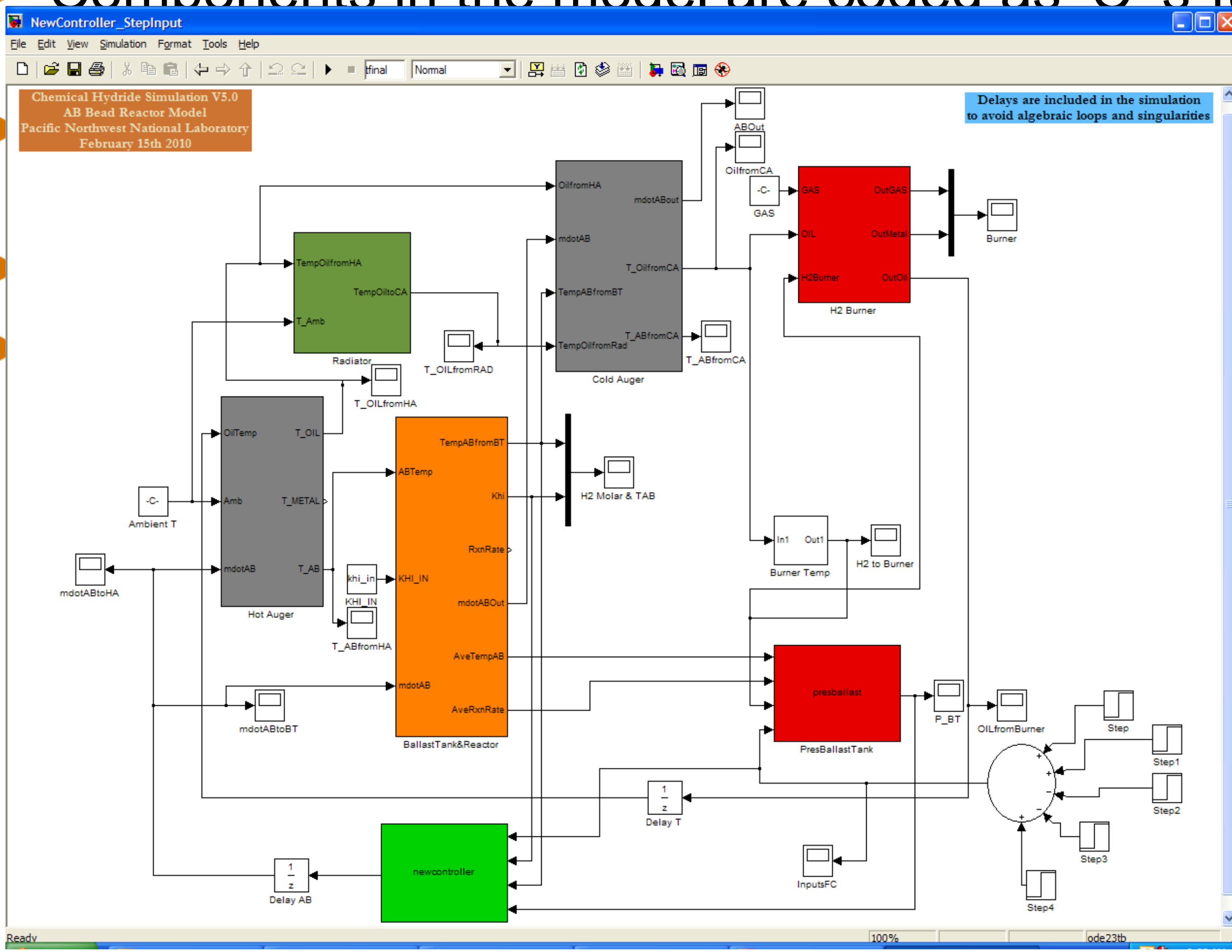
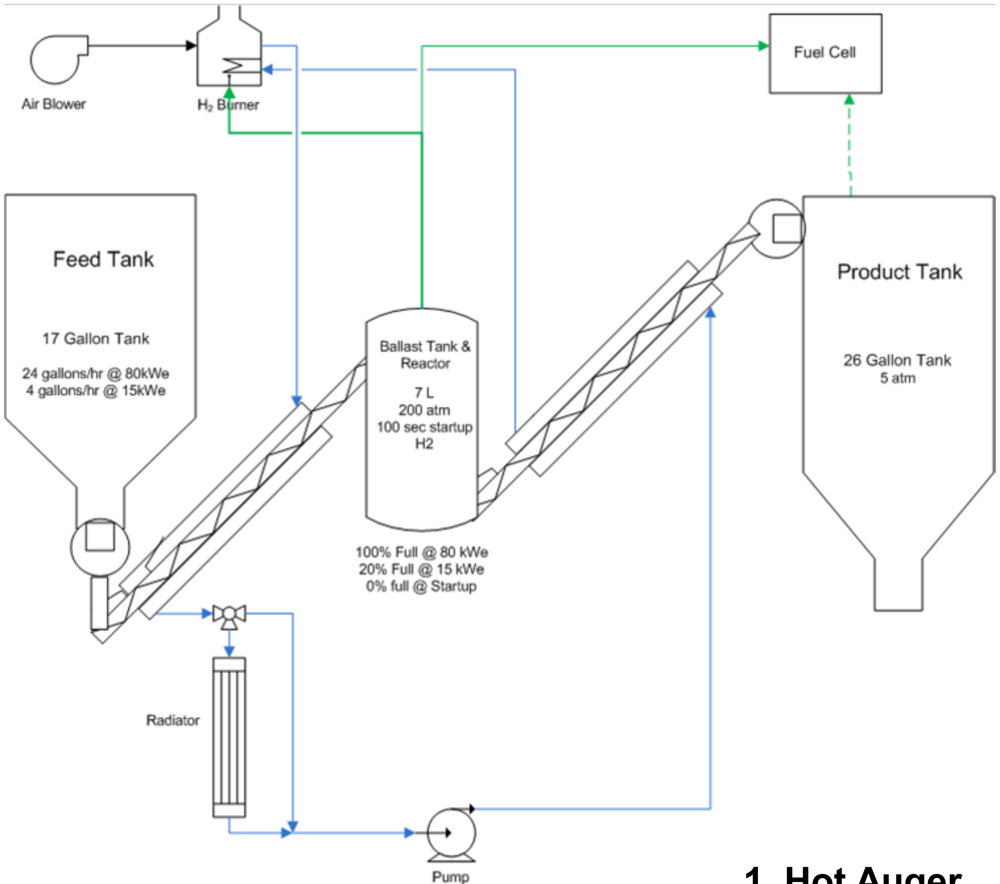


Baseline AB Bead Reactor System



- Developing, refining system concepts
- Intrinsic kinetic models developed
- Developing reactor sub-models for use in system model
- Investigate auger / reactor heat transfer coefficients
- Determine “rheology”, “stickiness” of reacting AB with and without additives (e.g., using DMA and/or rheometers)

Main components in the reactor system:

1. **Hot Auger**
2. **Ballast Tank & Reactor**
3. **Cold Auger**
4. **Radiator**
5. **H_2 Burner**
6. **Control System**

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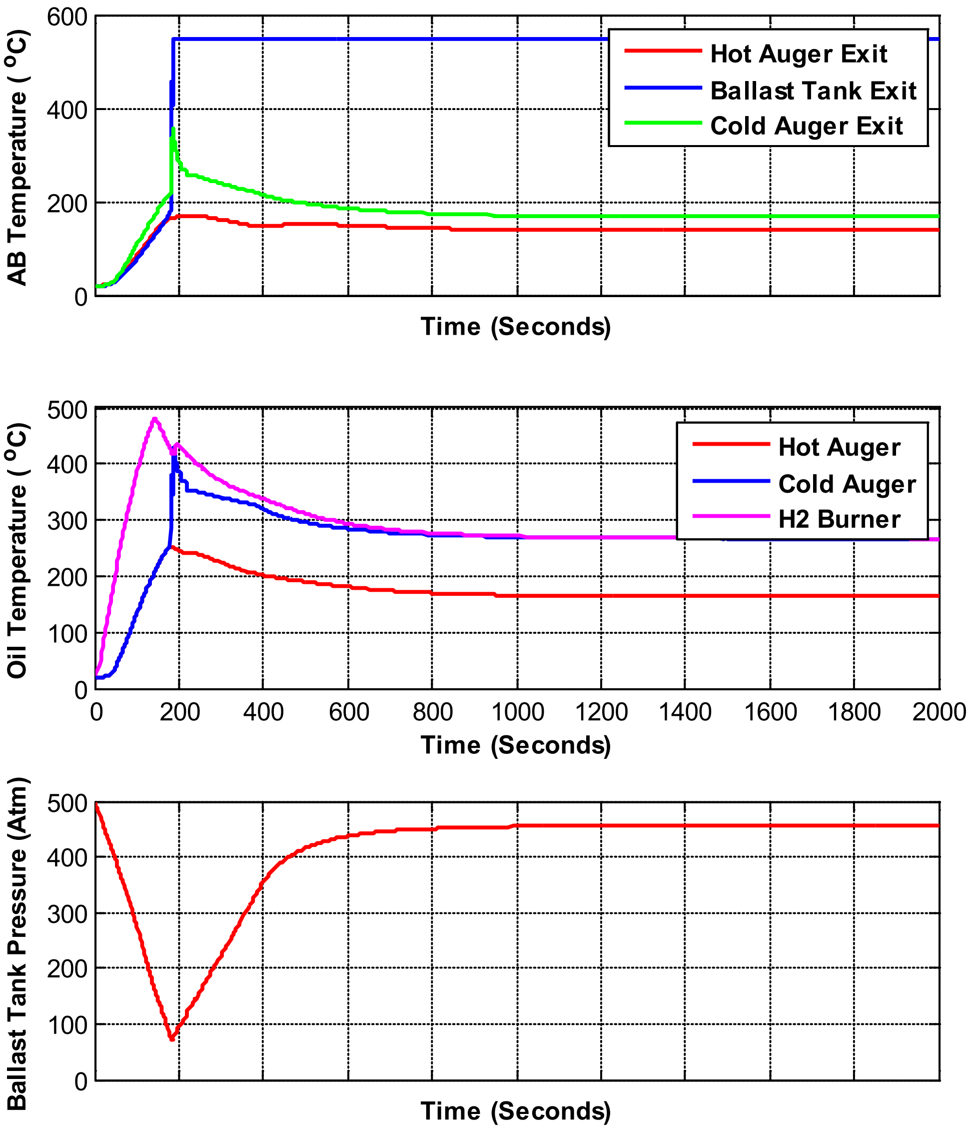
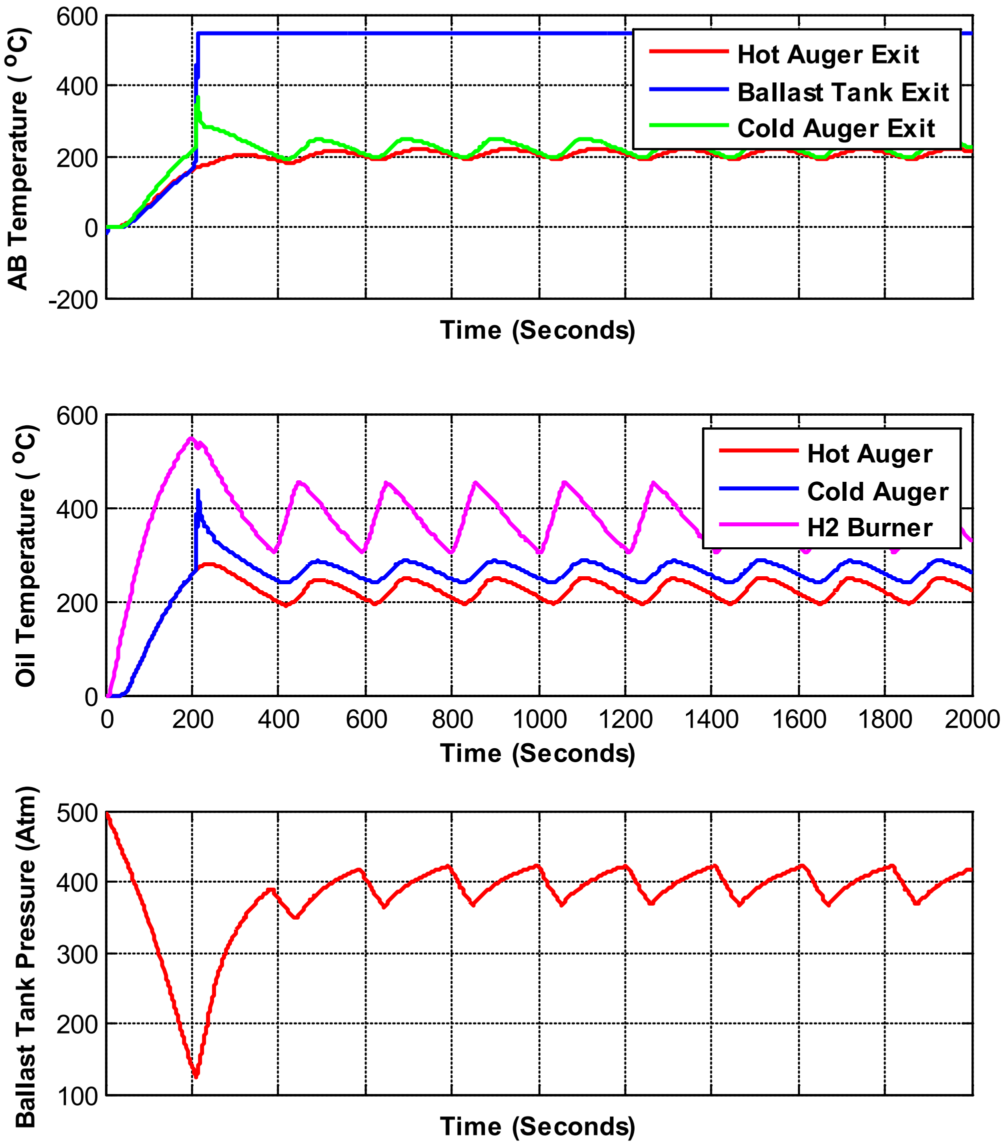
Simulation Results: Start-Up from 20°C



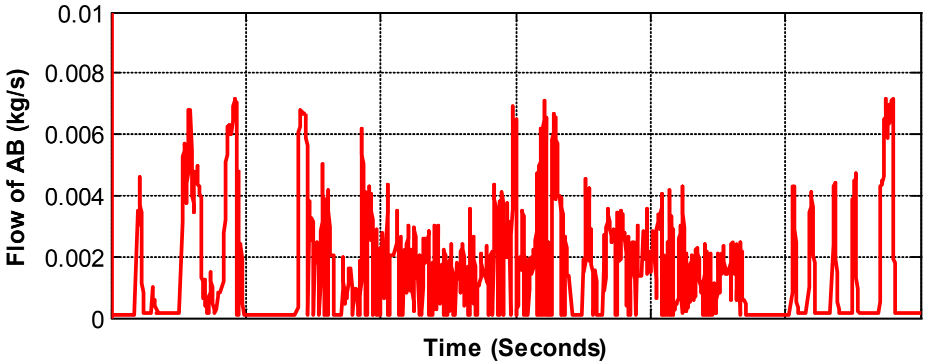
- Constant power 60 kWe
- AB begins to react at ~3 min
- Heat of reaction drives ballast tank reaction to maximum
- Reaction in ballast tank very small—will go away
- H_2 burner turns off at ~ 3 min
- Radiator not needed after hot auger, required for H_2 product
- Ballast Tank pressure drops to below 100 atm but rises again to 450 atm set point

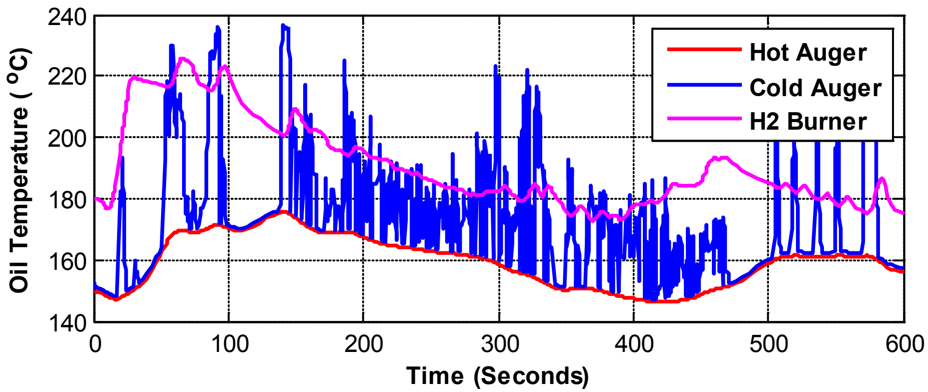
Simulation Results: Start-Up from -20°C (cold)

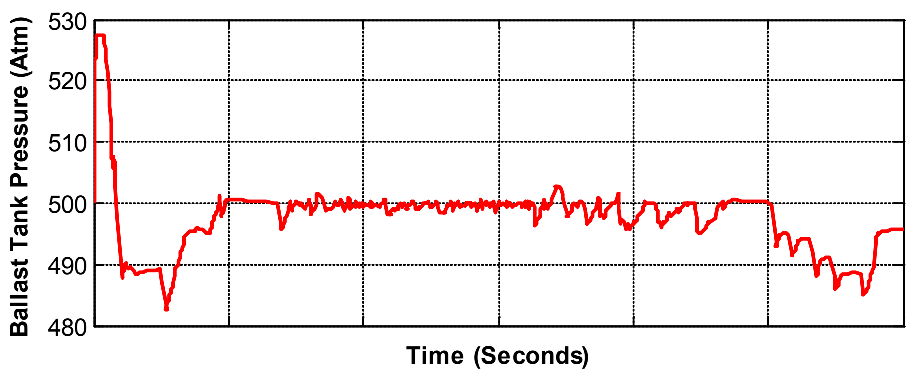


- Constant power 40 kWe
- AB begins to react at ~3.5 min
- Cold AB forces burner on after initial start-up
- Instability needs to be investigated
- Ballast Tank pressure drops to 100 atm but rises again to near 450 atm set point

Simulation Results: Drive Cycle after Warm-Up







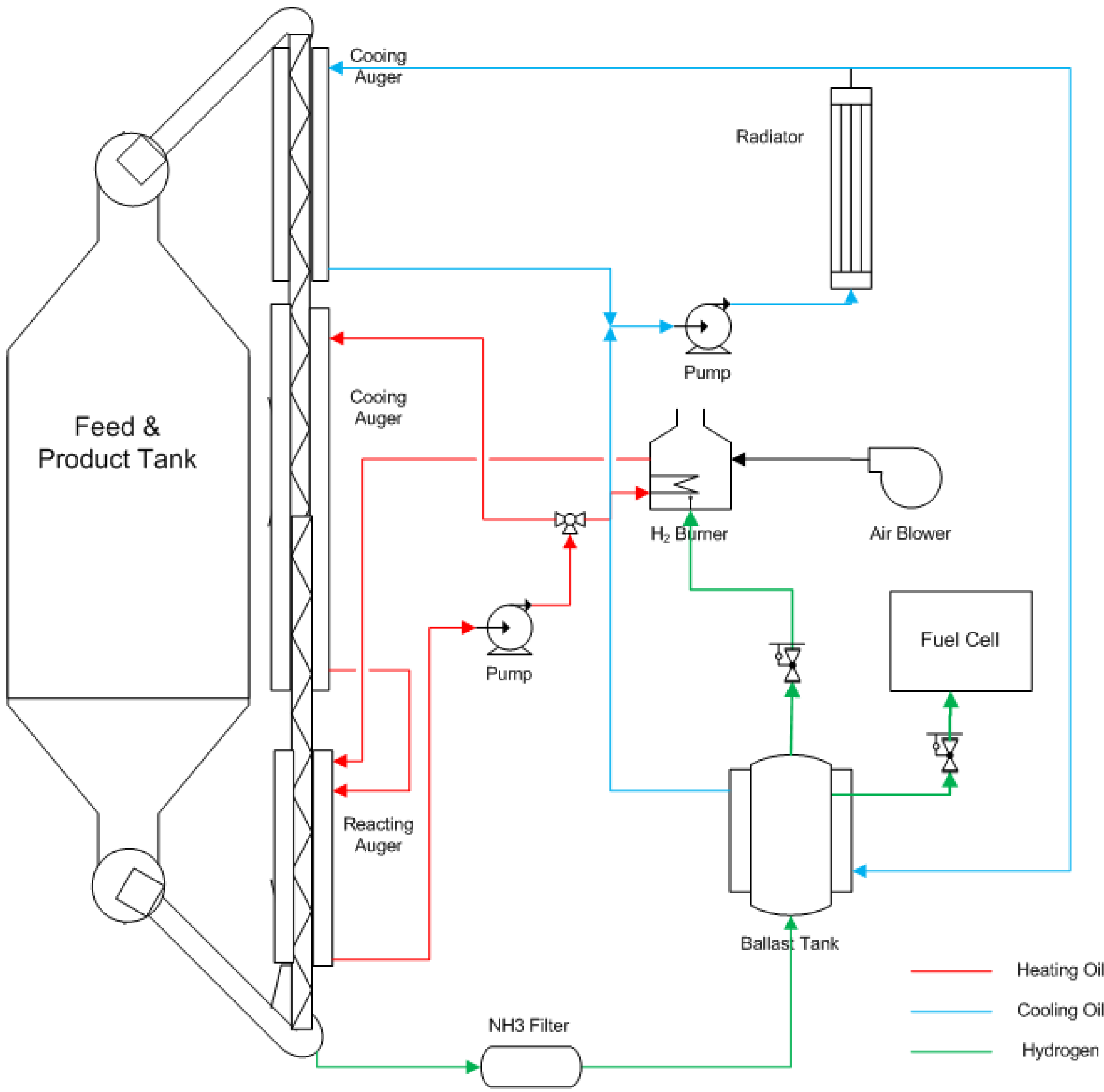
- US06 Drive Cycle with 0% Hybridization
- Pressure in Ballast Tank maintained ~ 500 atm
- Heated auger slowly cools at low flows
- H_2 burner turned on intermittently between 380 and 450 sec

System Weight and Volume Estimate

- Target: Total Mass 111 kg and Total Volume 178 liters

Component	Weight		Volume	
AB Storage	30.8	kg	0	L
Feed/Product Tanks	14	kg	140	L
Ballast Tank (carbon fiber)	29.7	kg	9	L
Hot Auger (steel)	10.8	kg	3.2	L
Cold Auger (steel)	20.2	kg	6.3	L
Burner/Blower	6.3	kg	5.7	L
Radiator	1	kg	1.8	L
NH_3 Filter	2.2	kg	2.7	L
Oil Piping/Pump/Tank	4.7	kg	3.5	L
<u>Valves/Actuators</u>	<u>5</u>	<u>kg</u>	<u>3.5</u>	<u>L</u>
Total	125	kg	176	L

Better Engineered Solution



- To address weight/volume constraints, a new design of the bead reactor is proposed
- Kinetics in the augers rather than ballast tank
- Combined Feed and Product Tank
- Better thermal control through multiple heat exchanger loops and through control logic.
- Hot hydrogen heats incoming AB feed

Materials Characterization

Accomplishments

- Materials Centers of Excellence recommended top storage materials
  - Based on multiple criteria
  - Available data and access to materials
- Materials properties of 12 materials posted on HSECoE Share point: MOR/Shared documents/Materials data base
  - Identified materials properties needed for modeling
  - Populated with literature and partner known and validated property data and kinetics
  - Gap analysis completed and plan established to augment data
- Screening criteria/Questionnaire created
  - Material must pass this rough assessment to be further considered
  - Provided to organizations who have a material of interest

HSECoE Materials Categories

	Tier 1 Developed Materials	*Tier 2* Developing Materials	Down-selected Materials
Adsorbents	AX-21	Pt/AC-IRMOF 8	MOF 177
	MOF 5		
Chemical Hydrides	$NH_3BH_{3(s)}$	$NH_3BH_{3(l)}$	
	AlH_3	$LiAlH_4$	
Metal Hydrides	$NaAlH_4$	$Mg(NH_2)_2$+MgH_2+2LiH	MgH_2
	2$LiNH_2$+MgH_2	$TiCr(Mn)H_2$	Mg_2NiH_4

- Developed Materials: System analysis is being performed on up-selected candidates and necessary engineering properties measured
- Developing Materials: Up-selected materials under performance evaluation and materials properties collected and measured if necessary
- Down-selected materials: Materials found to not improve system performance relative to up-selected materials, and thus not for further consideration

Storage Material Screening Criteria

Metal Hydrides

Chemical formula and reversible reaction formula

Capacity (wt% H_2 and kg H_2/L) as measured at what pressure (bar) and temperature (°C)

Absorption: give tempe

Desorption: give tempe

Enthalpy, ΔH (J/mol): fo

Crystal density (g/cm^3)

Cost raw material + add

Availability (g)

Chemical Hydrides

Chemical formula and decomposition reaction formula

Capacity (wt% H_2 and kg H_2/L) as measured at what temperature (°C)

Desorption: give temperature (°C)

Enthalpy of formation (J/mol)

Crystal density (g/cm^3)

Cost for raw material (precursor) (

Availability (g)

Adsorbents

Material and Synthetic Process

Capacity as independently validated maximum Gibbs excess capacity (wt% H_2 and kgH_2/L) as measured at what pressure (bar) and temperature (°C). Provide isotherms at RT and 77K.

Desorption: give temperature (°C) and rate (g H_2/s) to reach max desorption capacity

Hydrogen uptake: give temperature (°C), pressure (bar) and rate (g H_2/s) to reach max adsorption capacity

BET Specific surface area (m^2/g) and pore size distribution and/or bulk density (g/cm^3)

Cost for raw material (precursor) and estimate for processing ($/g)

Availability (g)

Questionnaire applied to $LiNH_2$:MgH_2 1:1

Chemical formula and reversible reaction formula

$LiNH_2 + MgH_2 = LiMgN + 2H_2$ etc

Capacity (wt% H_2 and kg H_2/L) as measured at what pressure (bar) and temperature (C) and cycle life (# of abs/des cycles and % capacity loss)

7.9wt% H2 adsorbed at ?C and ? bar; 5 cycles

Absorption at RT-250 C at 1-700 bar: give temperature (C), pressure (bar) and rate (g H_2/s) to reach max absorption capacity

?? Data not yet in data base, but in literature

Desorption at 80-250 C at 1-3 bar: give temperature (C), pressure (bar) and rate (g H_2/s) to reach max desorption capacity

?? Data not yet in data base, but in literature

Enthalpy, ΔH (J/mol) <50kJ/mol: for formation and/or reaction

33.5kJ/mol

Crystal density (g/cm^3)

2.388mg/m^3

Cost raw material + additive ($/g)

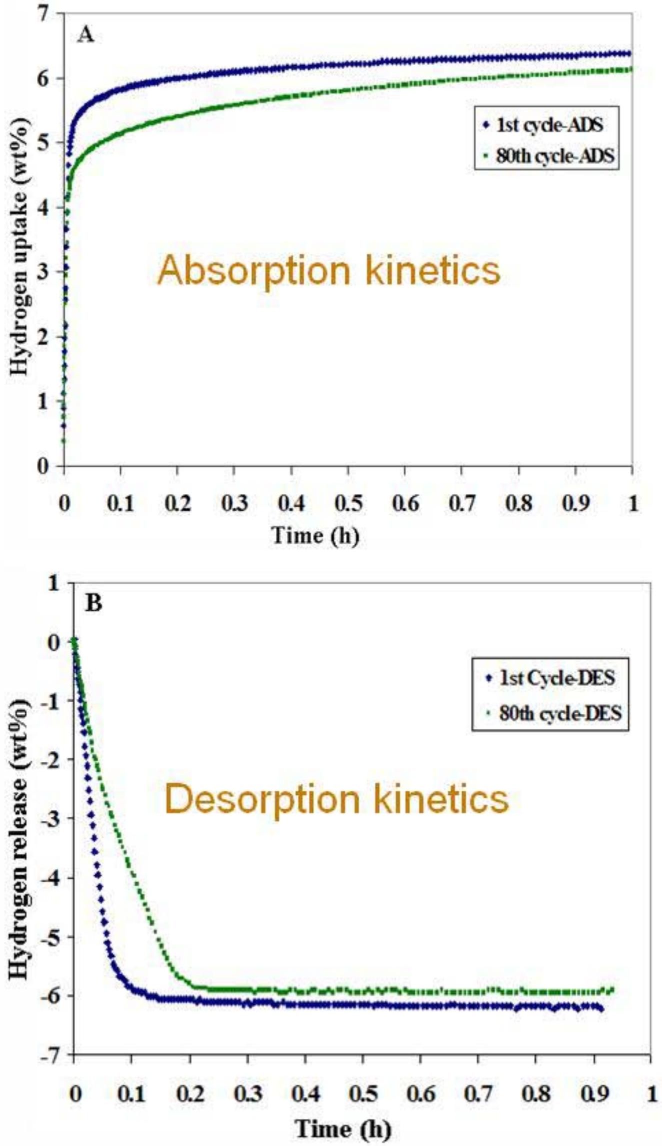
Availability (g)

Example: Data Base for Sodium Alanate

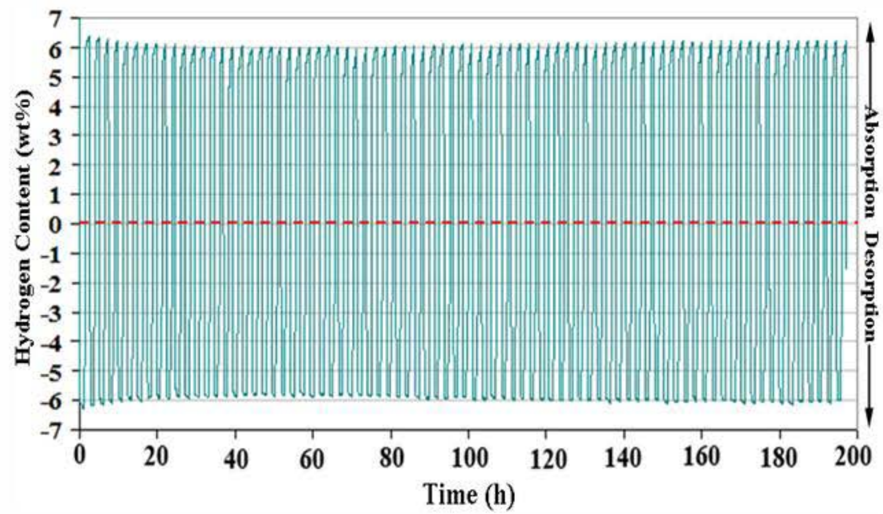
Category	Property	reported value	reference
	Composition	$NaAlH_4$+2m%$TiCl_3$+0.33m%$AlCl_3$+0.5m%$FeCl_3$	
	Catalyst	2m%$TiCl_3$+0.33m%$AlCl_3$+0.5m%$FeCl_3$	
	Impurities/Ratios	$NaAlH_4$: 86.3% $NaAlH_4$, 4.7%Na_3AlH_6, 7.5% free Al and 10.1% insoluble Al (in wt%).	Mosher et al. UTRC Final Report (2007)
Synthesis	**Method**	SPEX ball milling under nitrogen for 6 hours	Mosher et al. UTRC Final Report (2007)
Decomposition Pathways		$\boxed{NaAlH_4 \Leftrightarrow \frac{1}{3} Na_3AlH_6 + \frac{2}{3} Al + H_2 \Leftrightarrow NaH + Al + \frac{3}{2} H_2}$	hluwalia, R.K. (2007) Inter J of Hydro Energy **32**
	Intermediates	57.1 mol% NaH, 42.9 mol% Al	Srinivasan 377(2004)283
		35.3 mol% NaH, 54.6 mil% Al, 8.7% Na_3AlH_6, 1.3% NaCl	Srinivasan 377(2004)283
	Hydrogen Impurities	None	
Intrinsic properties	**Kinetic Model**	$\left(\frac{dC_j}{dt}\right)_{r_i} = D_i \exp\left(-\frac{E_i}{RT}\right) * \left(\frac{P_{e,i} - P}{P_{e,i}}\right) * (C_k)^{\chi_i}$	Mosher et al. UTRC Final Report (2007)
	D_i	**Needs to be calculated**	
	E_i	**Needs to be calculated**	
	$P_{e,i}$	**Needs to be calculated**	
	χ	**Needs to be calculated**	

Example: Data Base for Sodium Alanate

Category	Property	reported value	reference
			Final Report
			Final Report
			07) Inter J of gy **32**
			2004)283
			2004)283
			Final Report



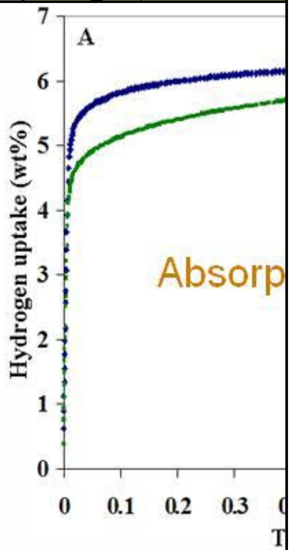
MgH$_2$+0.1TiH$_2$ 6wt% reversible at 300°C for 80 cycles. Kinetics remain similar.

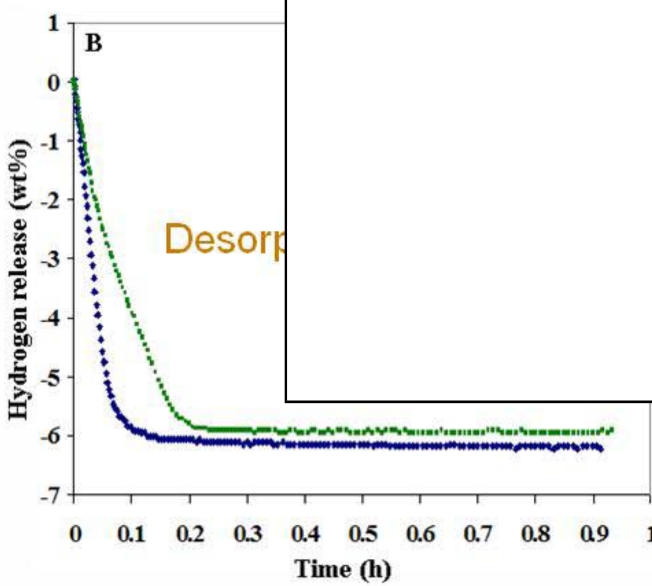


Jun Lu, Young Joon Choi, Zhigang Zak Fang, Hong Yong Sohn and Ewa Rönnebro, JACS 2010

Exam

Category





J. Graetz, et al. J. Phys. Chem. B (2005) 109, 22181-22185

TABLE 1: Isothermal Decomposition Rate Constants (s^{-1}) for α-, β-, and γ-AlH_3[a]

polymorph	k(60 °C)	k(80 °C)	k(99 °C)	k(120 °C)	k(138 °C)
α-AlH_3	1.35×10^{-6}	9.14×10^{-6}	4.21×10^{-5}	2.80×10^{-4}	1.39×10^{-3}
β-AlH_3	4.41×10^{-6}	1.36×10^{-5}	5.99×10^{-5}	4.88×10^{-4}	2.46×10^{-3}
γ-AlH_3	3.97×10^{-6}	1.18×10^{-5}	3.94×10^{-5}	2.71×10^{-4}	7.98×10^{-4}

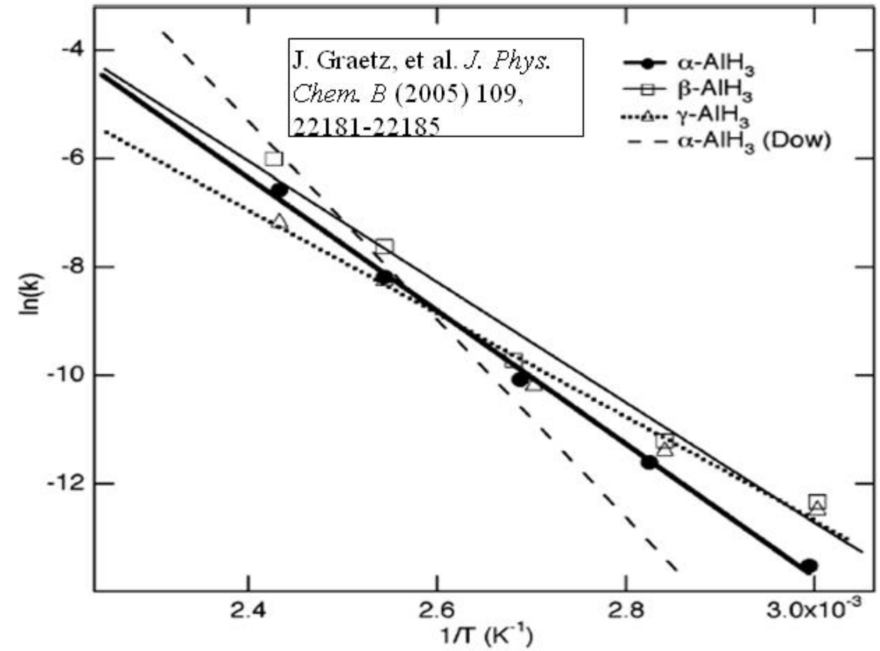


Figure 6. Arrhenius plot for large crystallites of α-AlH_3 (Dow)[4] and small crystallites of α-AlH_3, β-AlH_3, and γ-AlH_3. Reaction rates for the large crystallites of α-AlH_3 were measured at 135 °C ≤ T ≤ 160 °C and are extrapolated down to T ~ 60 °C.

Summary & Proposed Future Work

Collaborative Activities

Hydrogen Storage Engineering Center of Excellence	• Lincoln Composites - study of CF cost and pressure vessel design modeling • GM - design of structured media bed for MH • Ford – characterization of absorbent materials • UQTR - design and materials characterization of carbon absorbent • OSU - microarchetecture device concept development and thermodynamic analysis • UTRC - develop solutions for H_2 impurities filtering • LANL - AB system design and measure H_2 impurities • NREL - input for tank to wheels analysis and system cost models • SRNL - study AB reactivity and kinetics model development
SAWGG	• Participate in group discussions and analysis
Materials 'Reactivity' Program	• Khalil (UTRC) and Anton (SRNL) - understand reactivity properties of AB • Van Hassel (UTRC) - study impurities in H_2
Independent Analysis	• TIAX - provide design details for AB refueling cost and feasibility assessment, plus share cost parameters for system cost modeling

Summary of Accomplishments

- A representative *systems model of a AB based bead reactor system was developed* and successfully simulated in Matlab/Simulink environment.
- A COMSOL *transport model was developed for a bead and a block system*. The heat and mass transfer model used a simple reaction rate expression: (1) Bead reaction can occur within the auger that has been designed assuming a 200°C wall. (2) Heating the outside surface of a block can light off the reaction for the entire block.
- An improved *kinetic model has been developed and implemented* into the system model.
- *Hydrogen loss and impurities assessed for solid AB* as material is moved into and out of the pressurized reaction system.

Summary of Accomplishments (con't)

- Materials properties database established for HSECoE partners
- Screening criteria/Questionnaire created
- Engineering cost model structure established
- Studies and analysis of pressure vessels performed:
  - Metal hydride hybrid
  - Vessel material of construction sensitivity analysis
  - Liner material assessment
- Materials compatibility and reactivity studies started

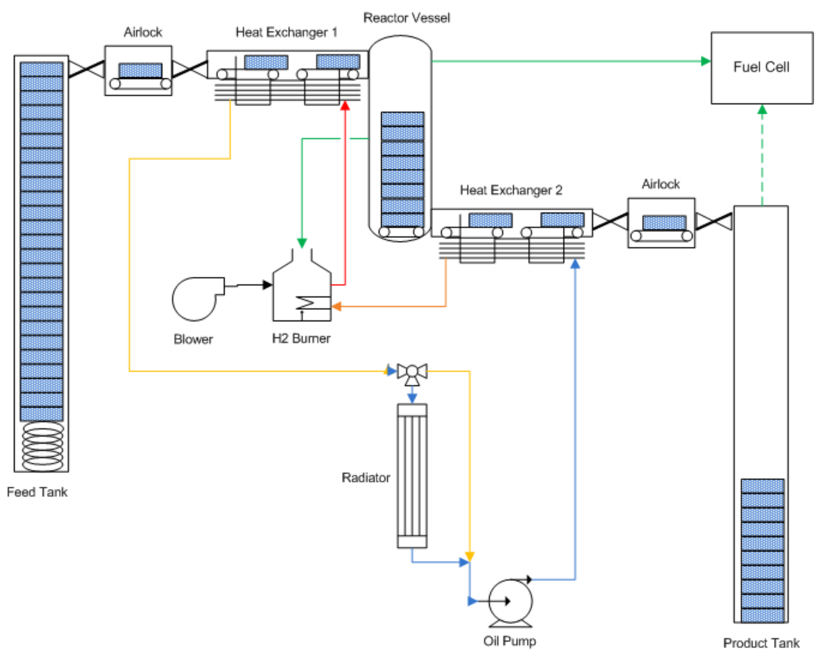
Future Work: Chemical Hydride System Design

- Future work includes implementation of the new bead reactor design in Matlab/Simulink and corresponding simulation analysis
  - Improve H2 Delivery Temperature
  - Increase Volumetric/Gravimetric Density
  - Include variable transport properties (ρ, Cp, k, zH2)
  - Address impurities and hydrogen losses in design
- Investigation of alternate materials for chemical hydride hydrogen storage.
- Implementation of the new kinetic model in Matlab/Simulink and corresponding simulation analysis
- Include temperature dependent transport properties into models as they become available. Modify kinetic model with higher temperature experimental data.

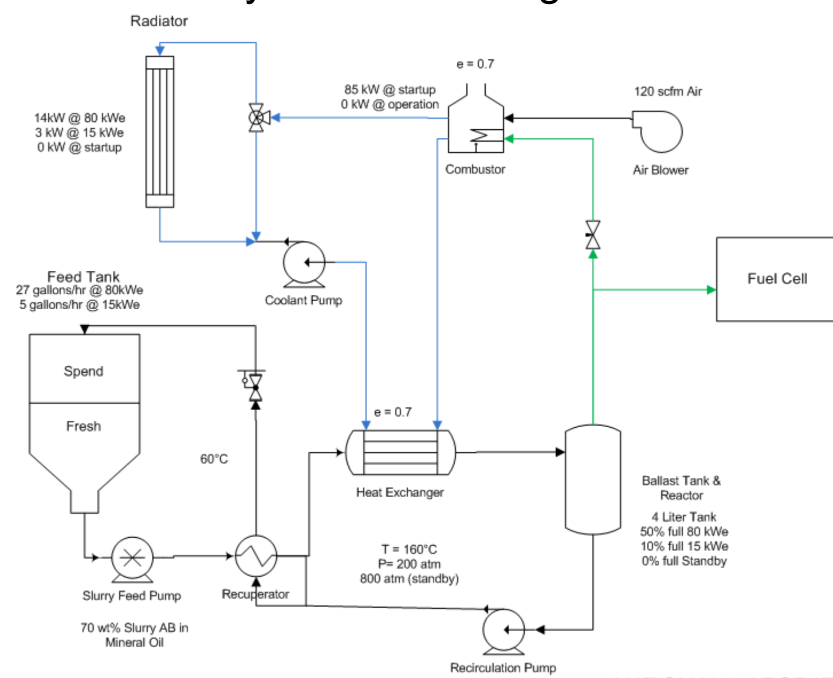
Future Systems to be Evaluated

- Materials to be Studied
  - Ammonia Borane ($NH_3BH_{3\,(s)}$) (Starting Material)
  - Alane (AlH_3)
  - Lithium Aluminum Hydride ($LiAlH_4$)
- Other System Configurations

Bulk Solids Configuration



Slurry Reactor Configuration



Future Work

- Complete system concept modeling efforts and provide initial component design for partner review
- Determine final reactor details and lock-in design
- Complete bulk kinetics modeling and validation studies
- Initiate heat exchanger modeling effort and provide initial component design for partner review
- Progression of cost model with system details and integrate component “catalog”
- Storage material bulk characterization

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Darrell Herling – Pacific Northwest National Lab, Principal Investigator
darrell.herling@pnl.gov, (509) 375-6905

Don Anton – HSECoE, Director
Monterey Gardiner – DOE EERE, Technology Development Manager