DOE Center of Excellence for Chemical Hydrogen Storage: PNNL Progress

Chris Aardahl, Tom Autrey, Maciej Gutowski, John Linehan, Scot Rassat, Don Camaioni, Dave Rector, Wendy Shaw, Ashley Stowe, Scott Smith Dave Heldebrant, Yongsoon Shin, Liyu Li, Jun Li

Pacific Northwest National Laboratory
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DOE Hydrogen Program Merit Review
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Project ST2

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project Start: 3-15-05
- Project End: 9-30-09
- Complete: 17%

Budget

- FY05: $900K
- FY06: $1200K

Barriers Addressed

- System weight & volume for 2010
- H_2 release rate
- Thermal management

Partners

Los Alamos National Laboratory, Rohm and Haas, Borax, Intematix, Northern Arizona University, Penn, The University of Alabama, Penn State, Millennium Cell, UCLA, University of California Davis, University of Washington

Objectives

- Identify and investigate chemical compounds that promise to meet DOE goals for storage density (gravimetric and volumetric), H_2 release rate, and fuel cost
  - Assist in evaluation of improved regeneration strategies for sodium borohydride (SBH)
  - Examine other boron systems such as the ammonia boranes
  - Propose and develop new chemical systems beyond boron
- Develop viable bench-scale chemistry from the Center into engineered approaches and demonstrate a viable storage system

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Approach

- Investigate chemical systems with high intrinsic capacity.
- Understand the kinetic limitations associated with release.
- Use state-of-the-art instrumentation and computational chemistry to determine thermodynamics and kinetics that govern cost within the fuel cycle.
- Use engineering tools to direct research activities
  - Multi-scale component models
  - Process models
  - Life cycle analysis
  - Semi-continuous to continuous bench-scale investigations
- Understand the trade offs regarding exothermic vs. endothermic hydrogen release

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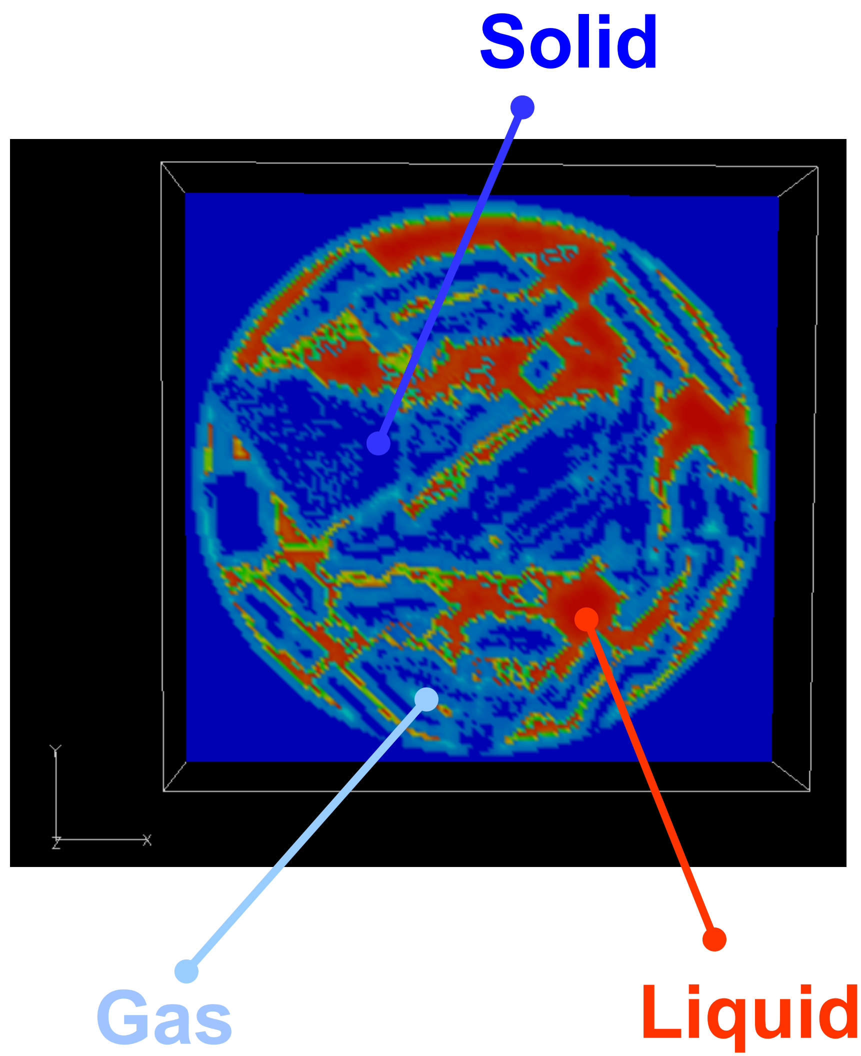
PNNL fit into Task Structure

- SBH (Capacity & Fuel Cost)
  - Building of multiscale reactor models to understand how higher concentration solutions can be processed
  - Data mining and bench scale experiments to assess alternative regeneration pathways
- B-N systems (Capacity, H_2 Rate, Thermal Management)
  - H_2 release from solid ammonia borane (AB)
    - Neat material
    - Scaffolded systems
  - Regeneration chemistry through in situ NMR
  - Fuel formulation stability
- Beyond ammonia borane (Thermal Management, Fuel Cost)
  - B-C-N systems
  - Coupled reaction systems
- Overall: Coordination of engineering activities within the Center

Accomplishments: Multi-scale Models

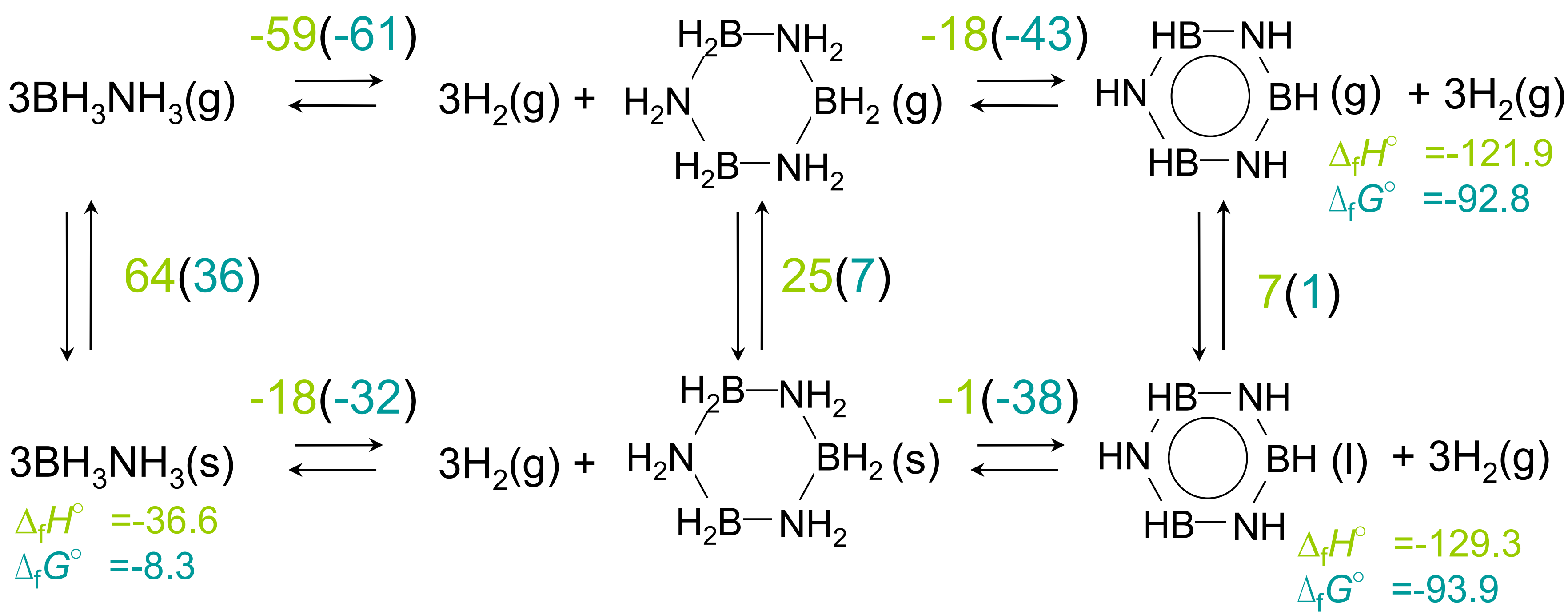
- Critical tool development for the Center
- Initial model based on SBH. Straightforward to adapt to other chemical systems
- Process
  - SEM cross-sections used to build 'virtual' reactor
  - Lattice-Boltzmann coupled to CFD
  - Kinetics taken from available databases
- Tool has been transferred to Millennium Cell
- PNNL will take lead on mod's for chemistries other than SBH.



Program Benefit: Reliable catalytic reactor models for future optimization

Accomplishments: More Complete Thermochemistry

ΔH° (ΔG°) in kcal/mol from Density Functional Theory calculations of *isodesmic* reactions and *key* experimental data from literature

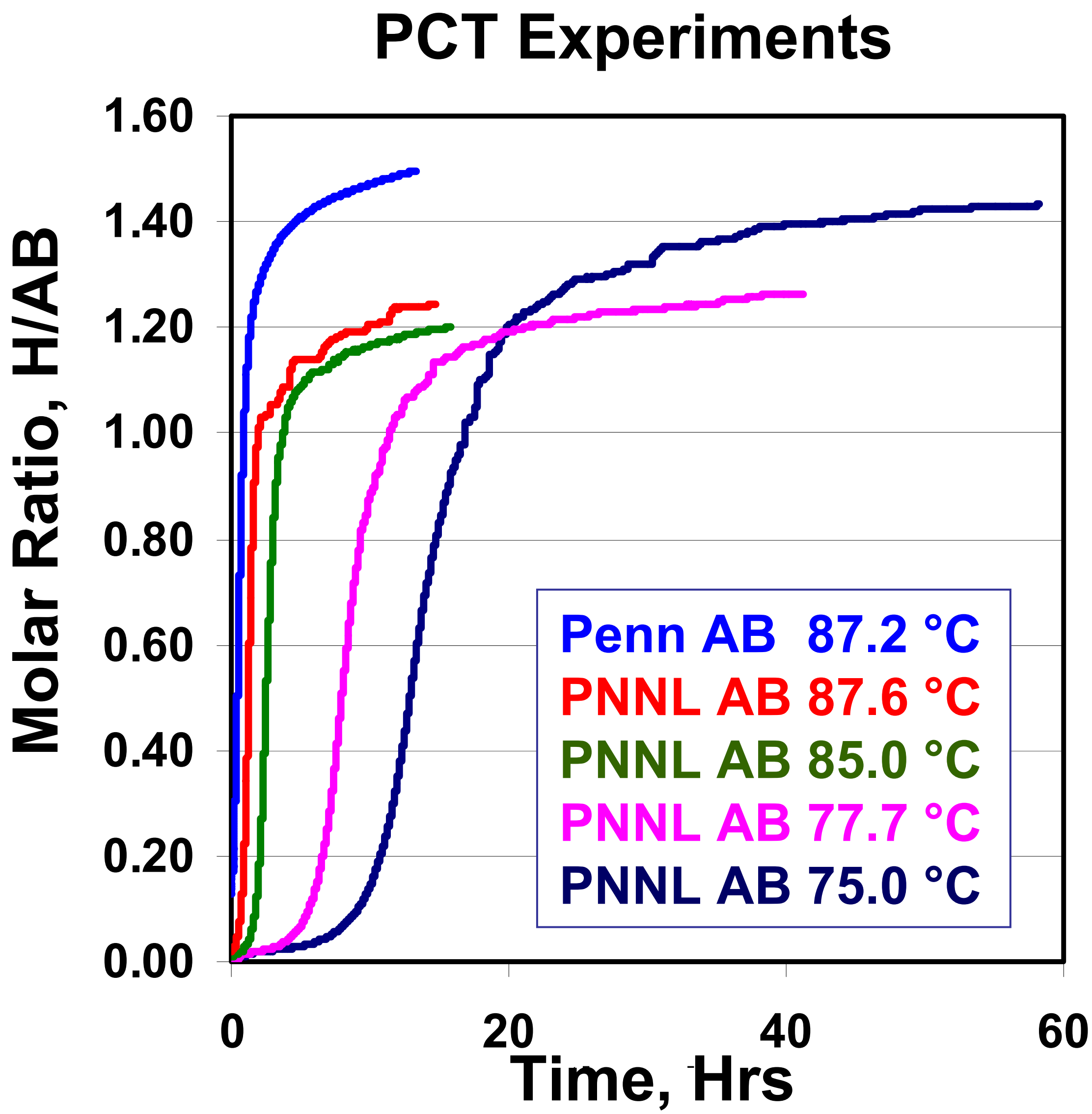


NIST Chemistry WebBook, NIST Standard Reference Database
Lange's Handbook of Chemistry
Wolf, G. in *W. E.-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials*, October 23-27, 2005, Bad Honnef, Germany
Leavers, D. R.; Long, J. R.; Shore, S. G.; Taylor, W. J. *J. Chem. Soc. (A)*, **1969**, 1580.

Program Benefit: Better assessment of thermal management & regeneration.

Accomplishments: Dehydrocoupling from AB

- Penn AB data showed faster kinetics. Could be due to impurities/source differences.
- Not all of the 1st equiv. is released until heating to 120°C.

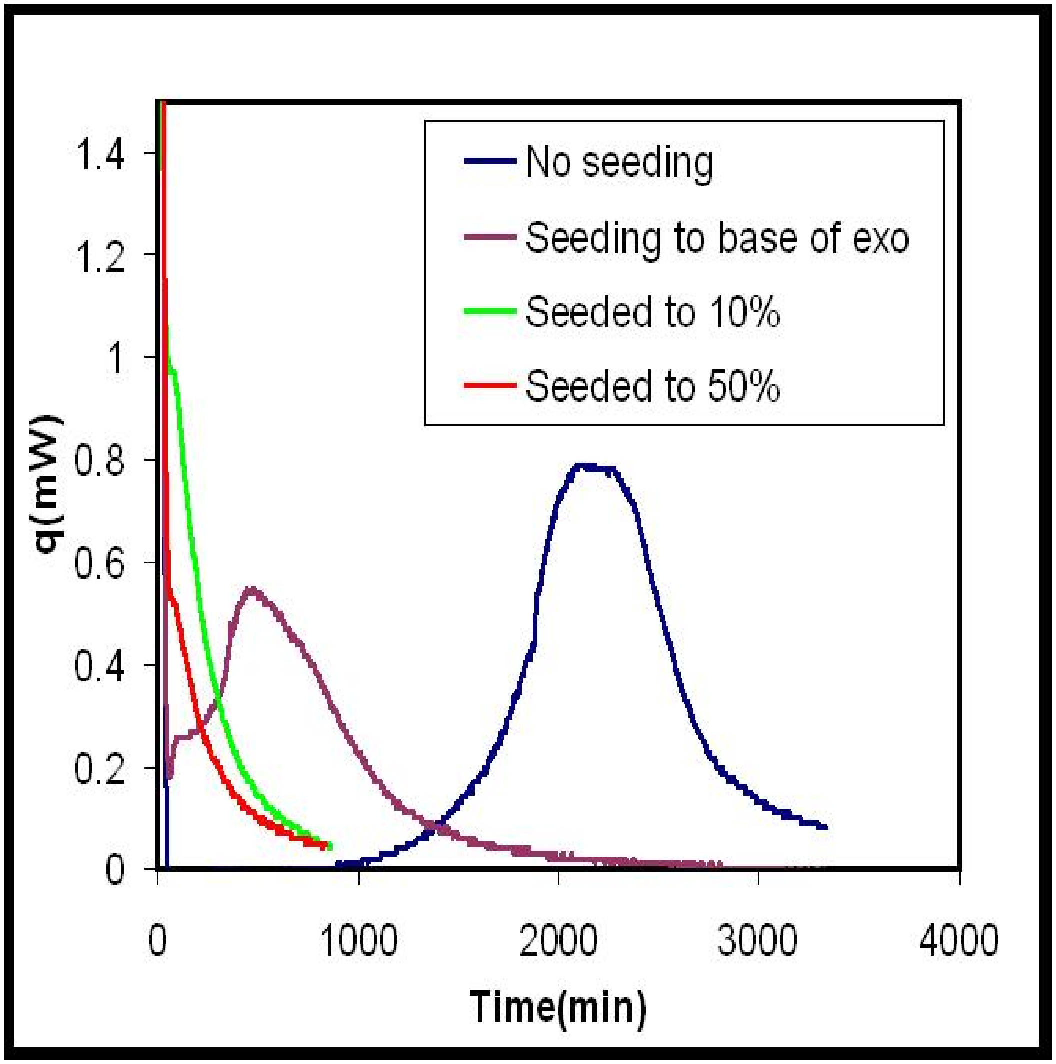


Long times: Penn 1.7 H/AB; PNNL 1.8H/AB

Program Benefit: Understanding release allows approach to full capacity.

Accomplishments: Seeding of Ammonia Borane

- Long induction period for hydrogen release is observed in neat AB.
- Indicates nucleation may govern process.
- Taking 'seeds' from partially spent AB and mixing them into fresh material results in much faster H_2 release.



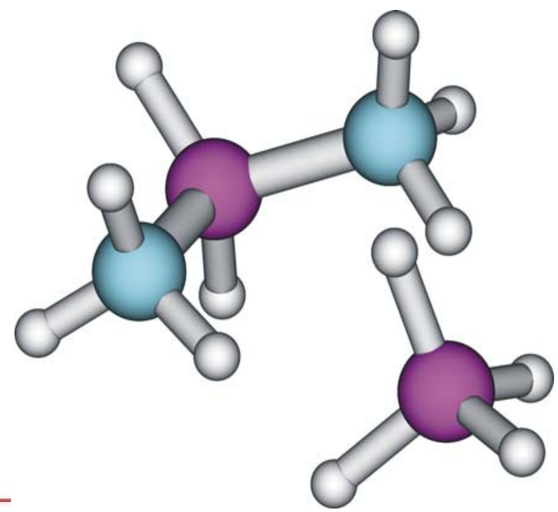
Accelerated kinetics for seeded samples

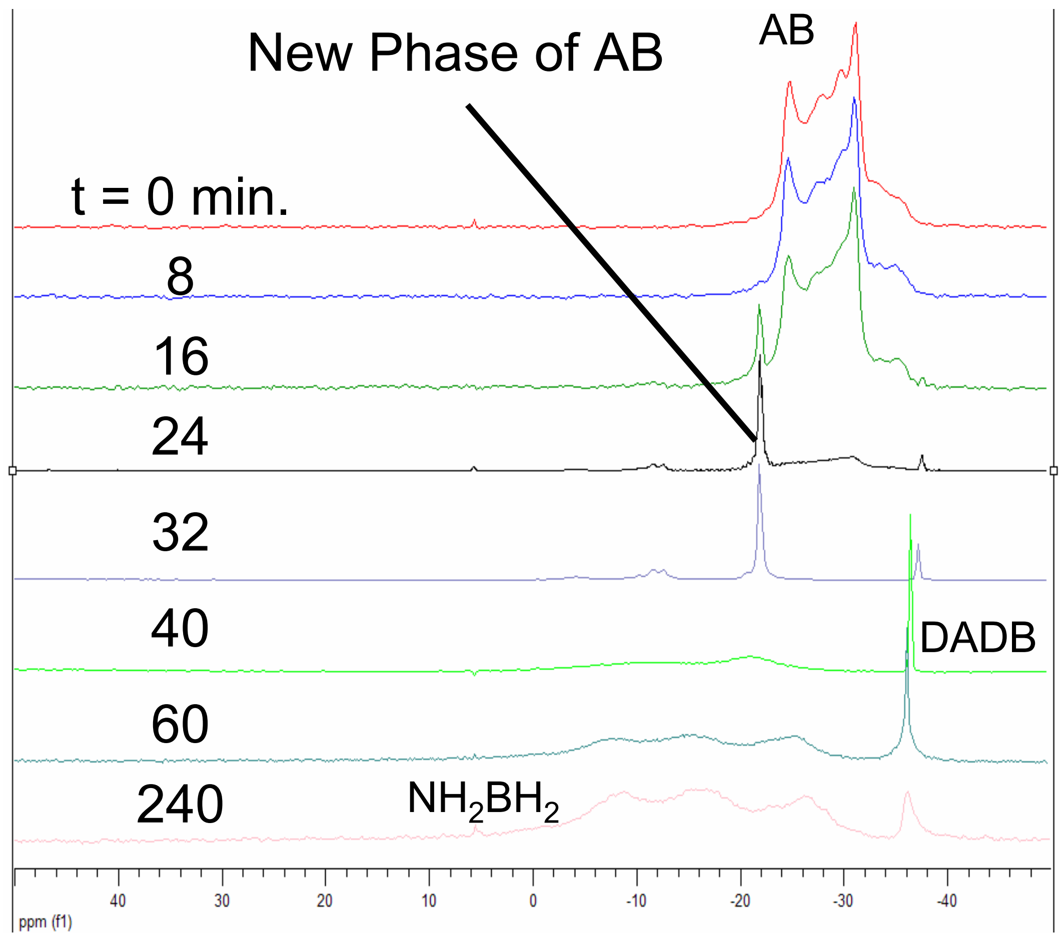
Program Benefit: More control over release will enable 2010 H_2 rate target.

Accomplishments: *In situ* ^{11}B NMR

- Reaction shows initial peak at -20 ppm (mobile AB phase), then growth of diammoniate of diborane (-36 ppm).
- One of these two species is likely the seed compound.

DADB: $[(NH_3)_2BH_2][BH_4]$





87.6°C, 7.05T, 300 MHz

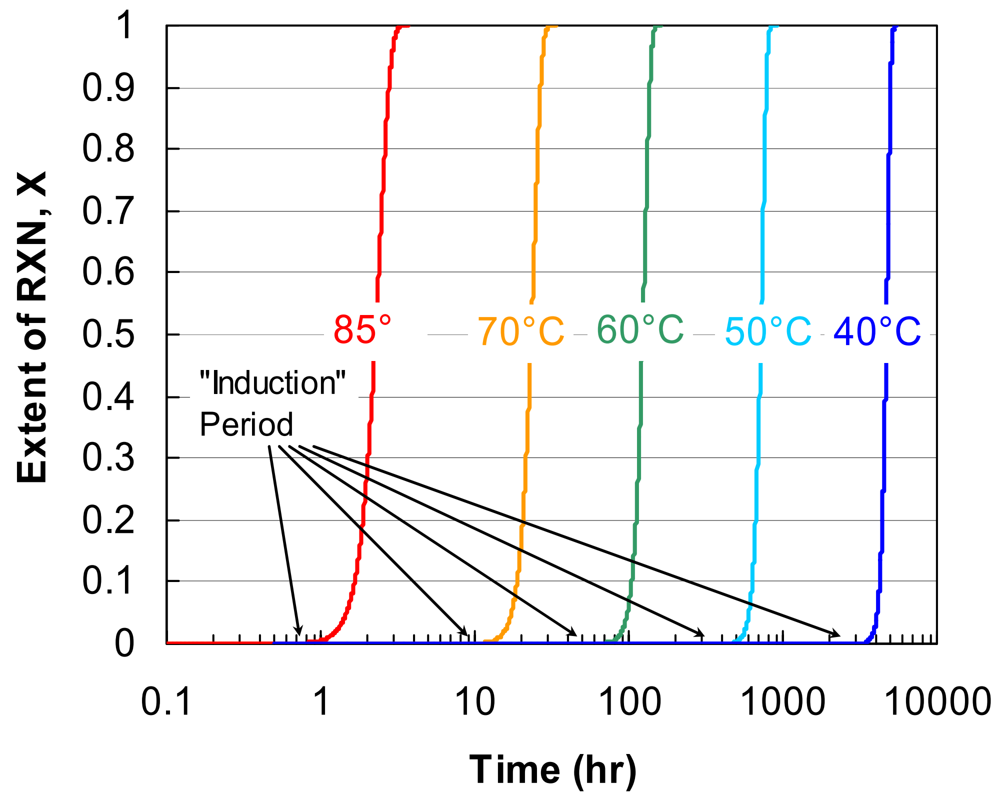
Program Benefit: Better understanding of options for fuel formulation.

Accomplishments: AB Stability

- 1st equivalent only – Avrami kinetics
- Isothermal DSC data used for initial fit of parameters [Wolf *et al.*, *Thermochimica Acta* 343, (2000) 19].
- Adiabatic assumed as a worst case
- AB bed properties
  - 1000 mol AB
  - No temperature gradients

Avrami Kinetics

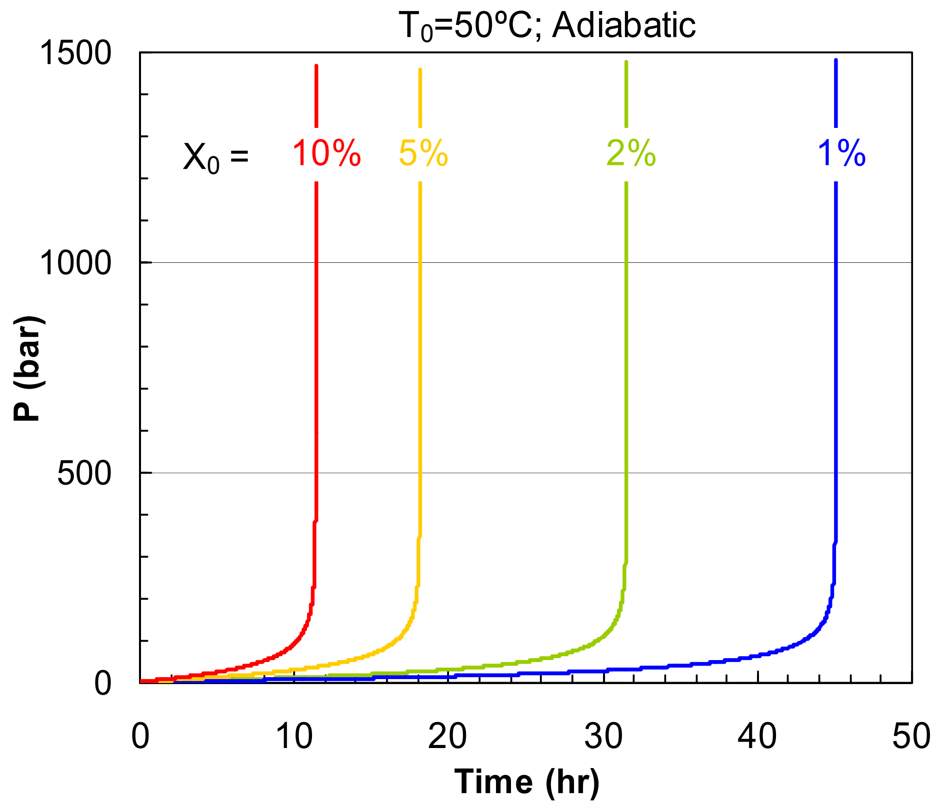
$$X = 1 - \exp[-(kt)^n]$$

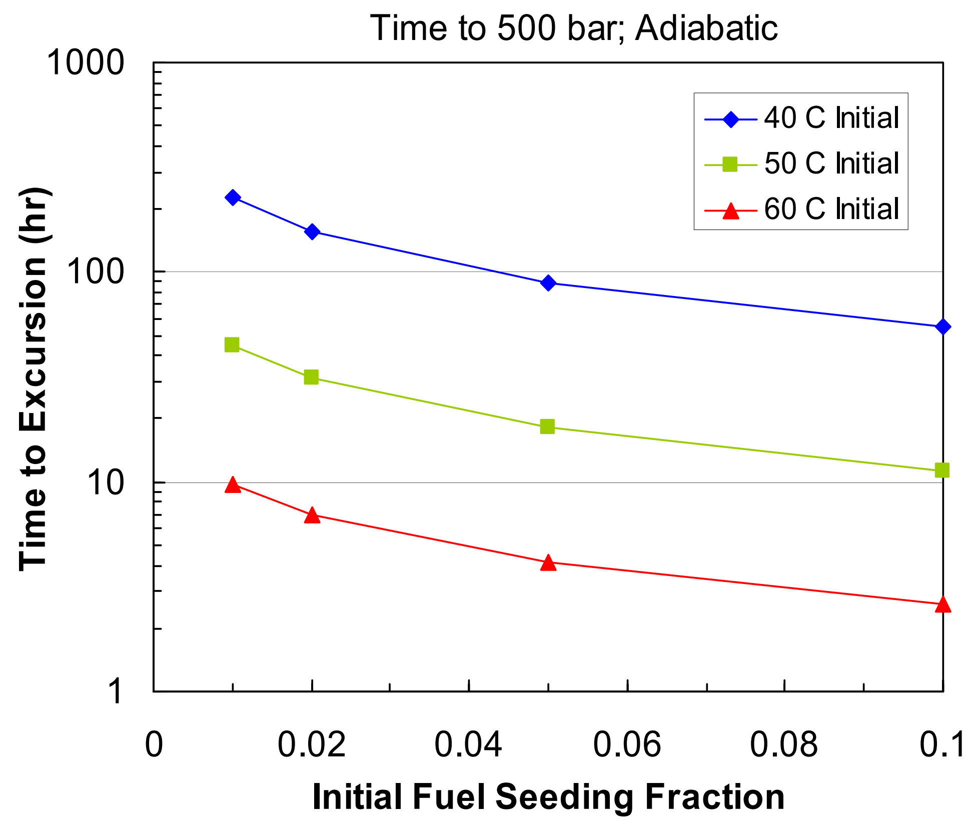


Program Benefit: Good baseline for handling thermal management.

Accomplishments: Impact of Seeding

- Model accounts for variation in H_2 release rate (dX/dt) as a function of temperature and extent of reaction (X), and the change in bed temperature due to heat of RXN
- Seeding or partial conversion of the AB fuel reduces the "induction" period

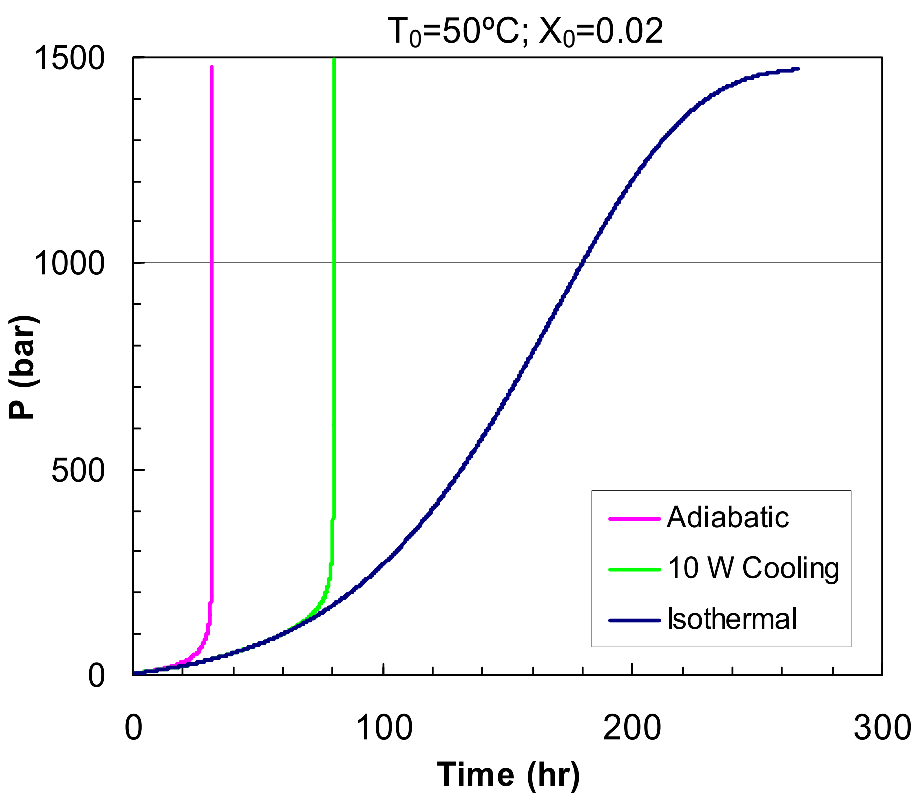


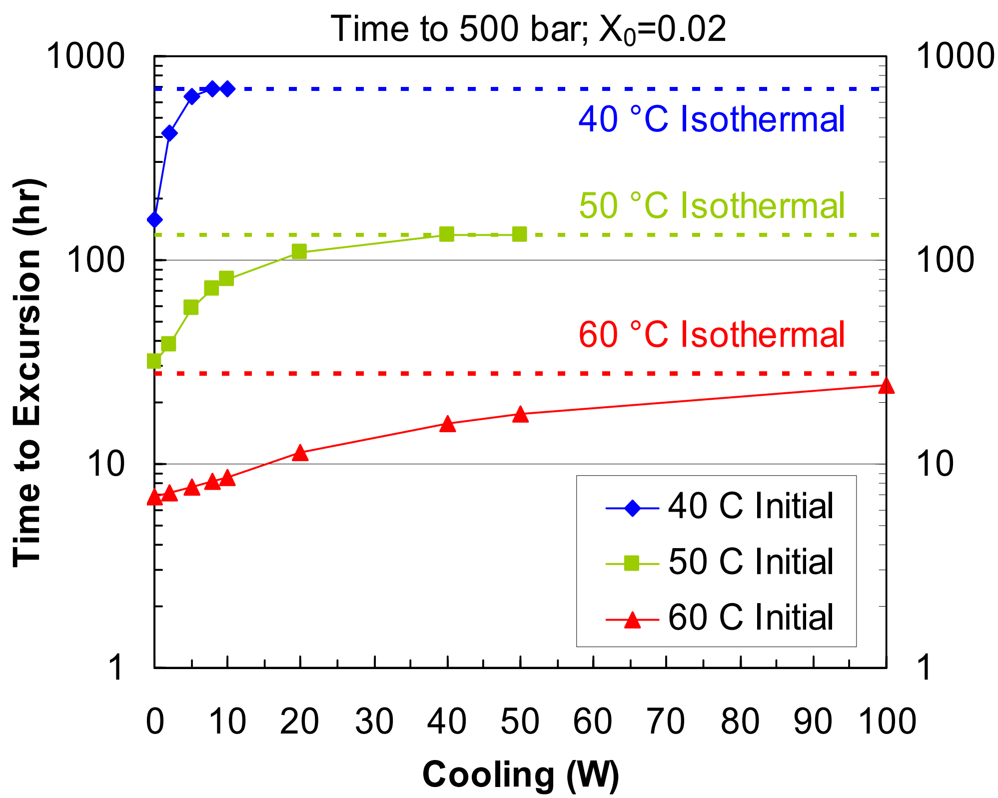


Program Benefit: Good baseline for handling thermal management.

Accomplishments: Heat Management

- Under adiabatic conditions, the AB bed temperature and reaction rate increases due to the heat evolved as H_2 is released (e.g., -22 kJ/mol)
- Small amounts of cooling and lower temperatures greatly increase the thermal stability of the packed AB bed (e.g., storage tank)
  - Computationally, cooling was not allowed to decrease T below the initial value





Program Benefit: Good baseline for handling thermal management.

Future Work

- Quantitative measurement of rates for seeded and unseeded materials. Extrapolation to obtain status vs. 2010 target.
- Quantitative measurements of release for the 2nd H_2 Equiv. on AB.
- Scaffold work
  - Impact of pore size/shape and phase
  - Impact of scaffold surface chemistry (as synthesized silica vs. treated silica) (**Milestone: 9/06**)
- Engineering studies: infrastructure for semi-continuous and continuous work
- Complete multi-scale model (**Milestone: 9/06**). Extend model to other systems such as AB. Build infrastructure for ChemCAD process models.
- Finish the stability study on ammonia borane and propose paths forward for heat management. Model serves as a general method for any exothermic system. Rohm & Haas helping with calorimetry to validate calculations.
- Regeneration of AB via chemical pathways (in situ NMR, then yield quantification)
- Computational and synthetic work on new systems.
- Develop go-no go criteria with Center (**Deliverable: 9/06**)

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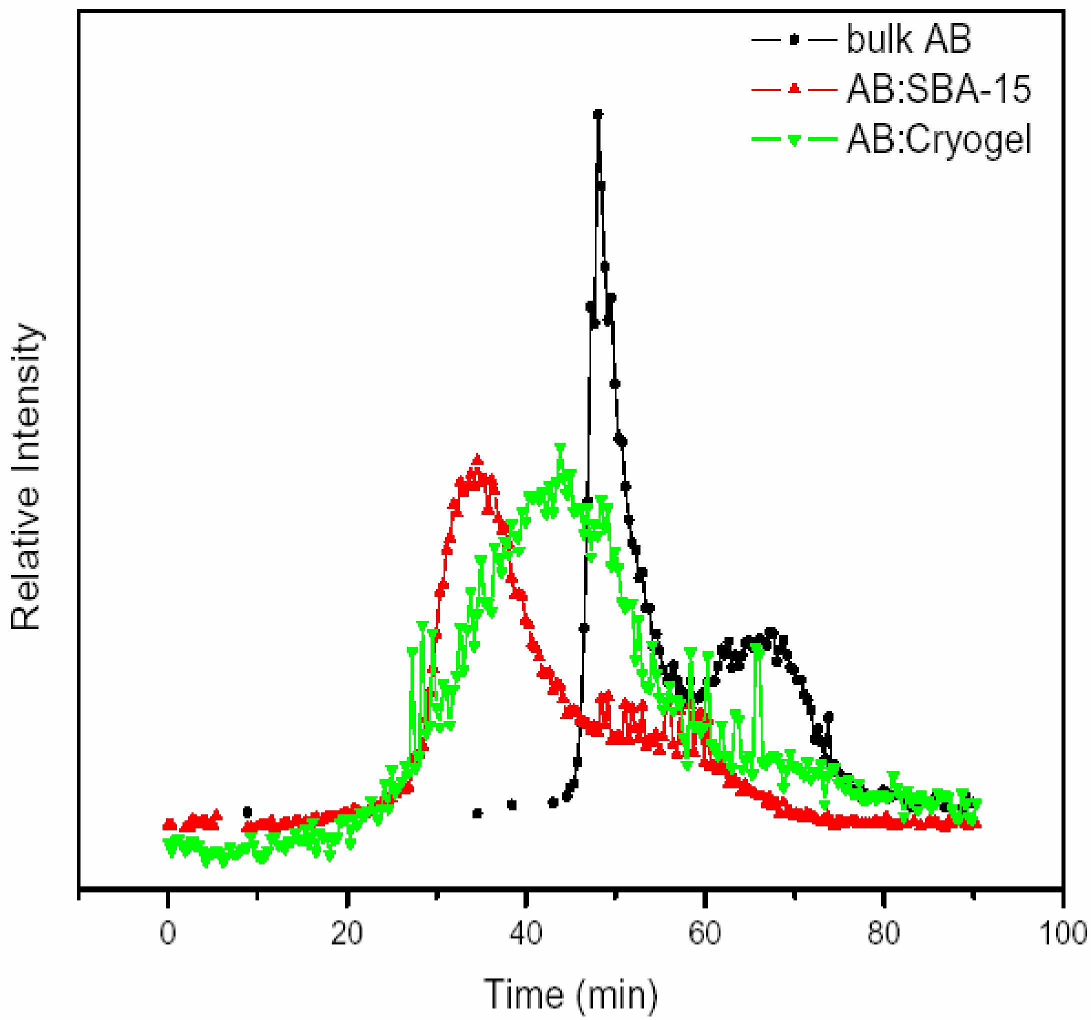
Future Work: AB in Scaffolds

- Preliminary data has been collected on carbon scaffolds.
- Driver for this work is to reduce the scaffold weight and drive closer to intrinsic H_2 density of AB.
- Enhancement of kinetics observed, but somewhat less of an effect than silica scaffold.
- Indicates that surface chemistry of the scaffold should be examined further.



Collaboration with University of Washington (Cao & Feaver)

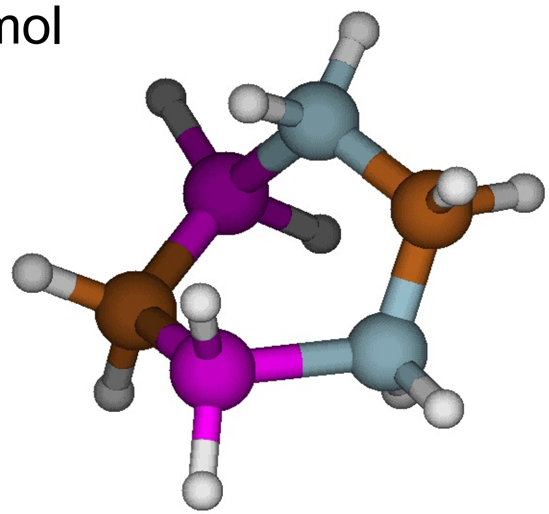
Future Work: B-C-N

- **Goal: Approaches for thermoneutral systems**
- **Borazine = exothermic: $B_3N_3H_{12} \rightarrow B_3N_3H_6 + 3H_2$**

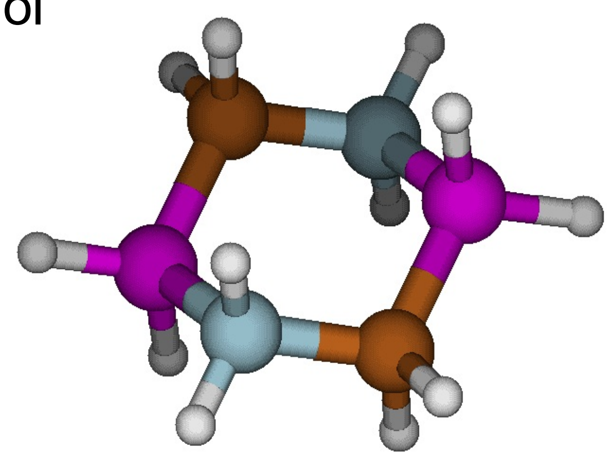
  ΔH= -18 kcal/mol; ΔG= -43 kcal/mol
- **Benzene = endothermic: $C_6H_{12} \rightarrow C_6H_6 + 3H_2$**

  ΔH= +49 kcal/mol; ΔG= +23 kcal/mol
- **C-B-N: $C_2B_2N_2H_{12} \rightarrow C_2B_2N_2H_6 + 3H_2$**

Case 1: C---C Symmetry
ΔH = -1 kcal/mol
ΔG = -27 kcal/mol



Case 2: No C---C Symmetry
ΔH = +31 kcal/mol
ΔG = -6 kcal/mol



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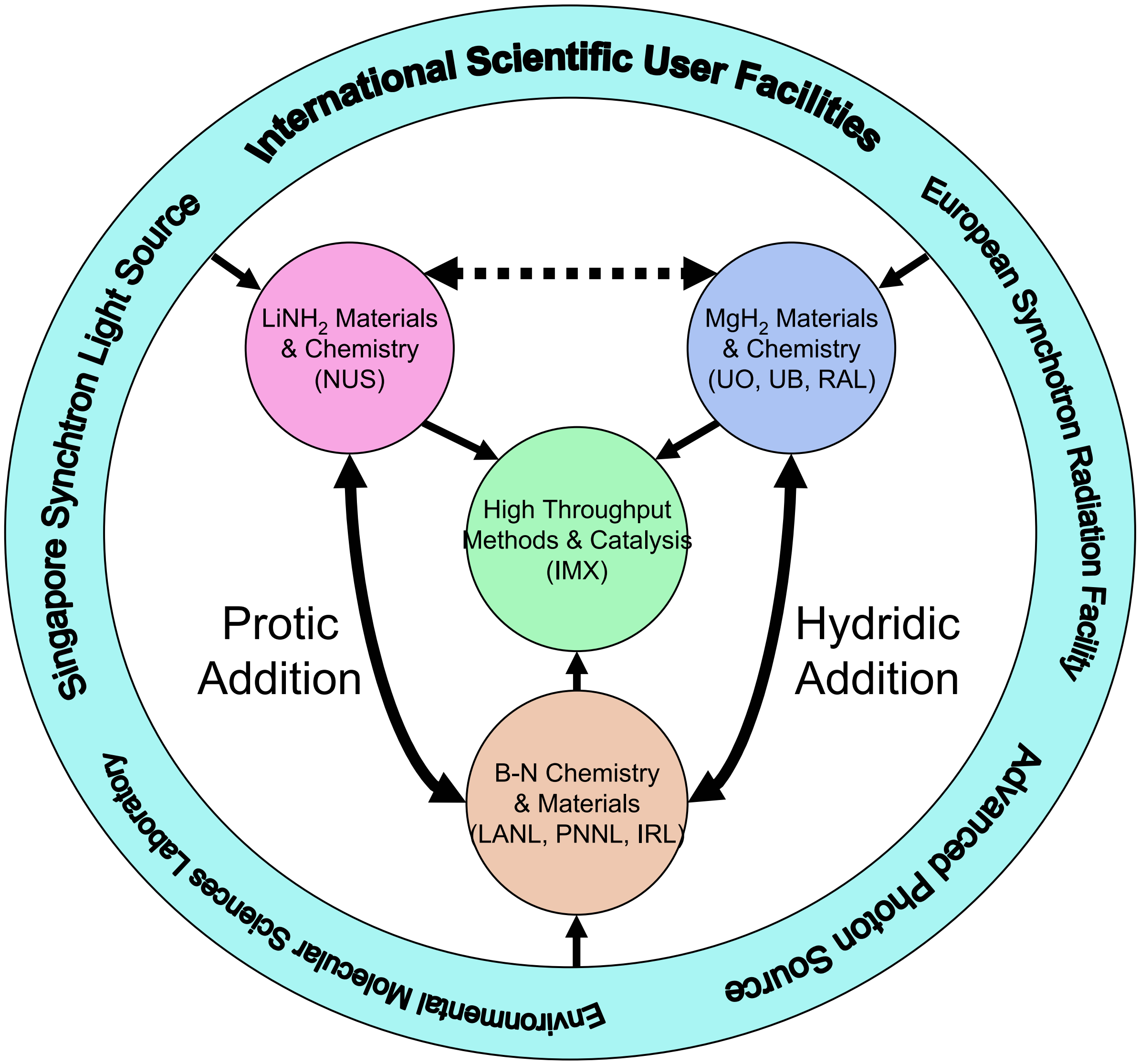
Future Work: IPHE Activities ($AB/LiNH_2/MgH_2$ systems)

- Proposal submitted for recognition in March 2006
- Decision on recognition in Fall 2006
- Collaborative activities are spooling up



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Critical Issues Moving Ahead

- Exothermic systems have to be thought of quite differently than endothermic systems. Hydrogen release must be performed apart from the primary fuel storage.
- Separation of hydrogen release from fuel storage indicates that a serious look at small-scale solids handling must be performed if something like powdered or even pelletized AB is to be used. What are the limits of existing handling methods?
- Off-board regeneration is also quite a shift from the on-board reversible systems. Will be difficult to estimate refueling cost without a significant amount of ‘off-board’ work. Fairly extensive process modeling, breadboard development and eventual piloting likely required.

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Summary

- Reliable multi-scale reactor models are close.
- With ‘exothermic’ hydrogen carriers, heat management must be addressed.
- AB releases hydrogen through a nucleation process. The release rate can likely be controlled through pretreatment of the formulation.
- Scaffolds are still very much of interest.
- Computations indicate that B-C-N chemistry is interesting.
- Complete thermodynamics are now available for the solid phase through a combination of measurements and a thorough look at the literature. Relationship between gas phase and condensed phase calculations is understood.
- This is the first review of the COECHS project for PNNL, therefore no review comments available from a year ago.

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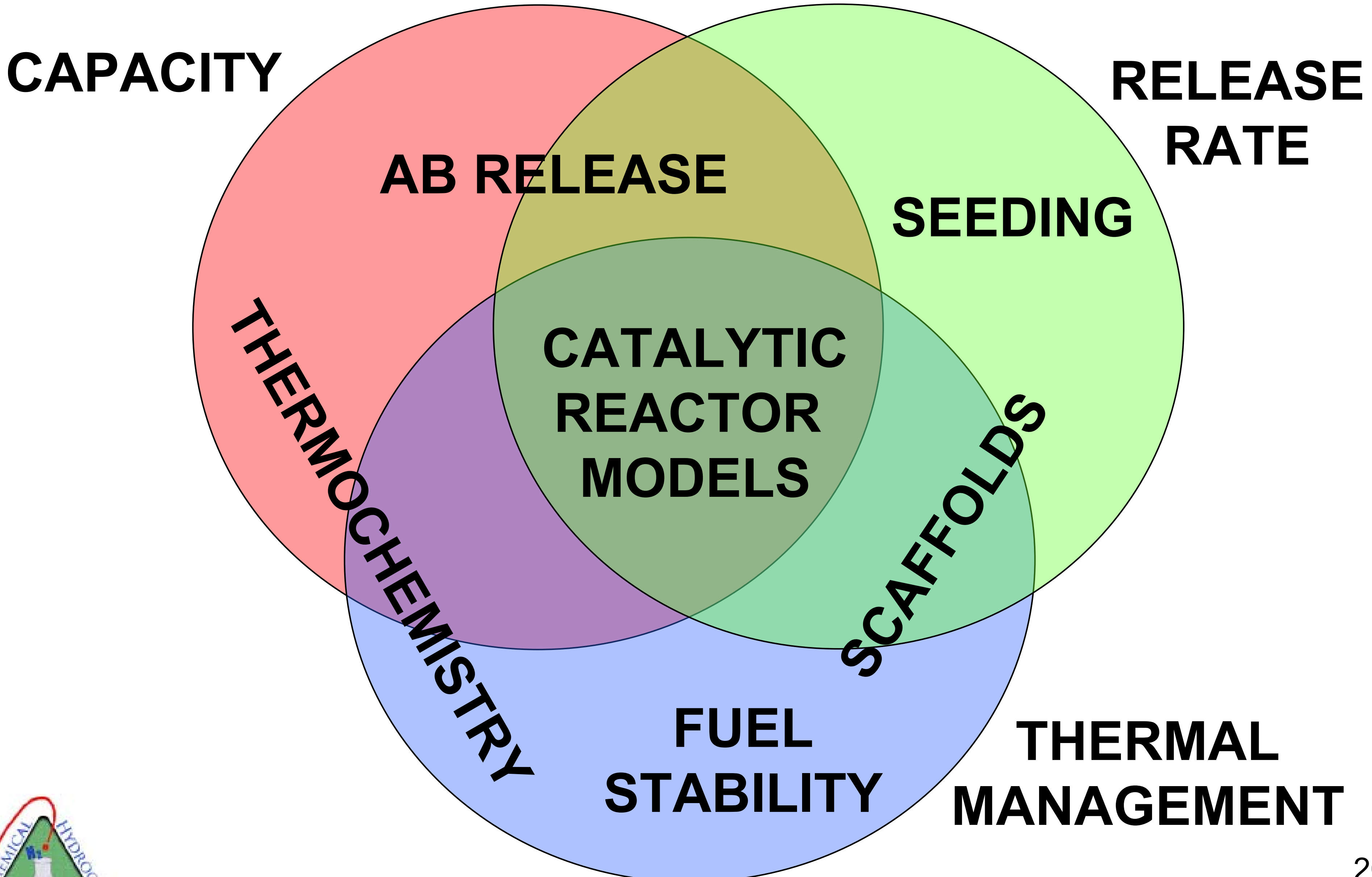
Impact on Reaching 2010 Targets



Summary Table

Total gH_2/g material (6 wt% system target for 2010 from US DOE)				
AB specifics	**Temp (^oC)**	**1st Equiv. 'material'**	**2nd Equiv. 'material'**	**Induction Period**
Neat Solid	86.5	**0.055**	No	Yes
Neat Solid	120	**0.065**	Yes	Yes
1:1 Silica Scaffold*	60	**0.032**	No	Reduced

* Reduction in volatile byproducts observed.

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Publications and Presentations

- *The Grand Challenge of Hydrogen Storage.* Maciej Gutowski, Simons Reunion Mini-symposium, Park City, UT 84060, June 19th, 2005.
- *Computational Studies of BNHx Materials.* M. Gutowski, R.A. Bachorz, T. Autrey, J. Linehan, Gordon Research Conference, Hydrogen-Metal Systems, Colby College, Waterville, ME, July 10-15, 2005.
- *The Challenge of On-Board Hydrogen Storage. Thermolysis of III-V Hydrogen-Rich Materials*, Maciej Gutowski, Anna Gutowska, Tom Autrey, John Linehan, Stanford University, Global Climate & Technology Project, August 4th, 2005.
- *Relative stability of (NH3BH3)2, [NH3-BH2-NH3]+ BH4-, and [BH3-NH2-BH3]- NH4+.* Maciej Gutowski, Rafal Bachorz, Tom Autrey, and John C. Linehan, the 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005; also Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem. **50** (2), 496 (2005).
- *Hydrogen Release from Ammonia Borane Mediated by a Nanoscaffold of Silica.* Maciej Gutowski, Rafal A. Bachorz, Tom Autrey, John C. Linehan, the 361st WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany, October 23-28, 2005.
- *The Challenge of On-Board Hydrogen Storage. Theoretical and Experimental Studies of BNHx (x=8-2) Materials.* Maciej Gutowski, Heriot-Watt University, Department of Chemistry, Edinburgh, UK, December 02, 2005.
- *Understanding of hydrogen storage in the NBHx materials through computational studies.* Maciej Gutowski, Rafal A. Bachorz, Jun Li, Greg Schenter, Shawn Kathmann, Tom Autrey, John Linehan, Anna Gutowska, Wendy Shaw, 231 ACS National Meeting, Atlanta, Georgia, March 26-30, 2006.
- *Hydrogen Storage in HNBH Systems.* Liyu Li, Benjamin Schmid, R. Scott Smith, Bruce D. Kay, John Linehan, Wendy Shaw, Nancy Hess, Ashley Stowe, Craig Brown, Luke Daemen, Maciej Gutowski & Tom Autrey. Materials Research Society Meeting, San Francisco, April **2006**

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Publications and Presentations

- *Amine Boranes for Chemical Hydrogen Storage*. Tom Autrey & Maciej Gutowski. Hydrogen Initiative Symposium sponsored by The Energy Center, Purdue University, West Lafayette, IN, USA April, **2006.**
- *Mechanistic studies of molecular hydrogen formation from borane ammonia complexes.* R. Scott Smith, Bruce D. Kay, Liyu Li, Nancy Hess, Maciej Gutowski, Wendy Shaw, John Linehan, Ashley Stowe, Benjamin Schmid & Tom Autrey. Carnegie Insitute, Washington DC, February, **2006**.
- *On-board Hydrogen Storage -- Breakthroughs and Barriers*. Tutorial: Materials Research Sociey Fall 2005. Tom Autrey, Weifang Luo, Phil Parilla. http://www.mrs.org/meetings/fall2005/tutorial_a.html
- *Novel Approaches for On-board Chemical Hydrogen Storage*. Tom Autrey, Anna Gutowska, John Linehan, Liyu Li, R. Scott Smith, Bruce D. Kay, Yongsoon Shin, Wendy Shaw, Nancy Hess, Benjamin Schmidt. Presented at the International Partnership for the Hydrogen Economy – Hydrogen Storage Technology Conference, Lucca, Italy, June 22nd, **2005**.
- *Controlled Hydrogen Release From Ammonia Borane Using Mesoporous Scaffolds*. Anna Gutowski, Benjamin Schmid, Liyu Li, R. Scott Smith, Bruce D. Kay, John Linehan, Wendy Shaw, Nancy Hess, Yongsoon Shin, Maciej Gutowski & Tom Autrey Presented at the American Physical Society Meeting, Los Angeles, March **2005**.
- Research Challenges for the Hydrogen Economy; Hydrogen Storage. Presented at New York City College, April 4th **2005**, Tom Autrey.
- *Hydrogen gets onboard*, RSC Chemistry World, March 2006, Maciej Gutowski & Tom Autrey http://www.rsc.org/chemistryworld/Issues/2006/March/HydrogenOnBoard.asp

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