Center of Excellence for Chemical Hydrogen Storage: PNNL Tasks and Collaborations

Chris Aardahl, Tom Autrey, Maciej Gutowski, John Linehan, Scot Rassat, Mike Thompson

Pacific Northwest National Laboratory

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Project STP3

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start: FY 2005
- Finish: FY 2009
- Percent Complete: New

Barriers

- Barriers addressed
  - Weight and Volume Density
  - Efficiency and Cost
  - System Life Cycle Assessment

Budget

- Total Proposed: $6.1M
  - All DOE share
- FY05: $900K

Partners

- Los Alamos NL, UCLA, UC Davis, Univ. Penn, Penn St. Univ., Univ. Washington, Univ. Alabama, N. Arizona Univ., Millennium Cell, Rohm & Haas, US Borax, Intematix

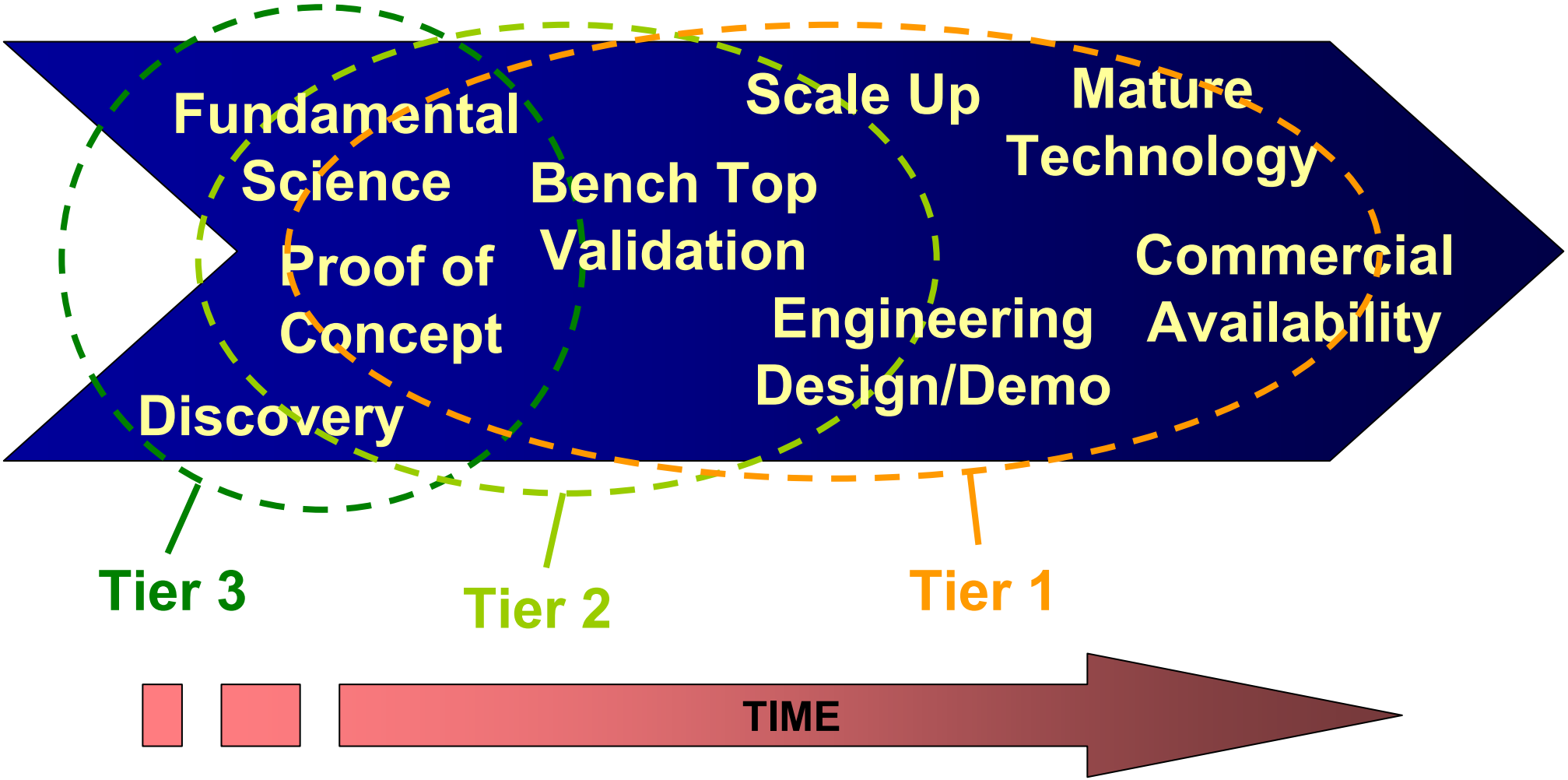
Objectives

- The objective of PNNL's portion of the project is to advance chemical hydrogen storage to meet the DOE targets in 2010 through collaborative projects with the Center members.
  - Computational assessment of novel approaches to chemical hydrogen storage. Computations of energetics of new compounds to make preliminary assessment of storage efficiency.
  - Synthesis and investigation of new compounds for high gravimetric and volumetric storage density. Understanding thermodynamics, kinetics, and catalysis associated with these new systems.
  - Engineering scale studies to assess performance of compounds in hydrogen delivery systems.
  - Life cycle inventory to assess regeneration energy requirements.
  - Demonstration of a 1 kg storage system.

Center Tier Structure

- Tier I (Hydrolysis): Regeneration of B-H bonds from B-O thermodynamic wells:
  - Millennium Cell, Rohm & Haas, US Borax, Penn State, Alabama, PNNL, LANL
- Tier II (Thermolysis): Avoid water and thermodynamic sinks in B-H systems. Alternative boron approaches include chemistry of complex boranes (B_xH_y), and the BN and BCNP systems:
  - Penn, Penn State, UCLA, Washington, Northern Arizona, Alabama, Intematix, PNNL, LANL
- Tier III (Thermolysis beyond B): Develop concepts for coupled endo/exothermic reactions, nanomaterials, and thermodynamic control by heteroatom substitution:
  - UC Davis, Alabama, Intematix, PNNL, LANL
- Center Core Capabilities
  - Computational Chemistry (PNNL, LANL, Alabama)
  - Core Engineering (PNNL, Millennium Cell, Rohm & Haas)
  - Core Science & Complex instrumentation (PNNL, LANL)
  - IP management (IP Management Committee)
  - Safety (PNNL, LANL, Northern Arizona)
  - Center coordination, technical planning (LANL)

Development Pipeline
(Center Spans a Range of Maturity)



Approach

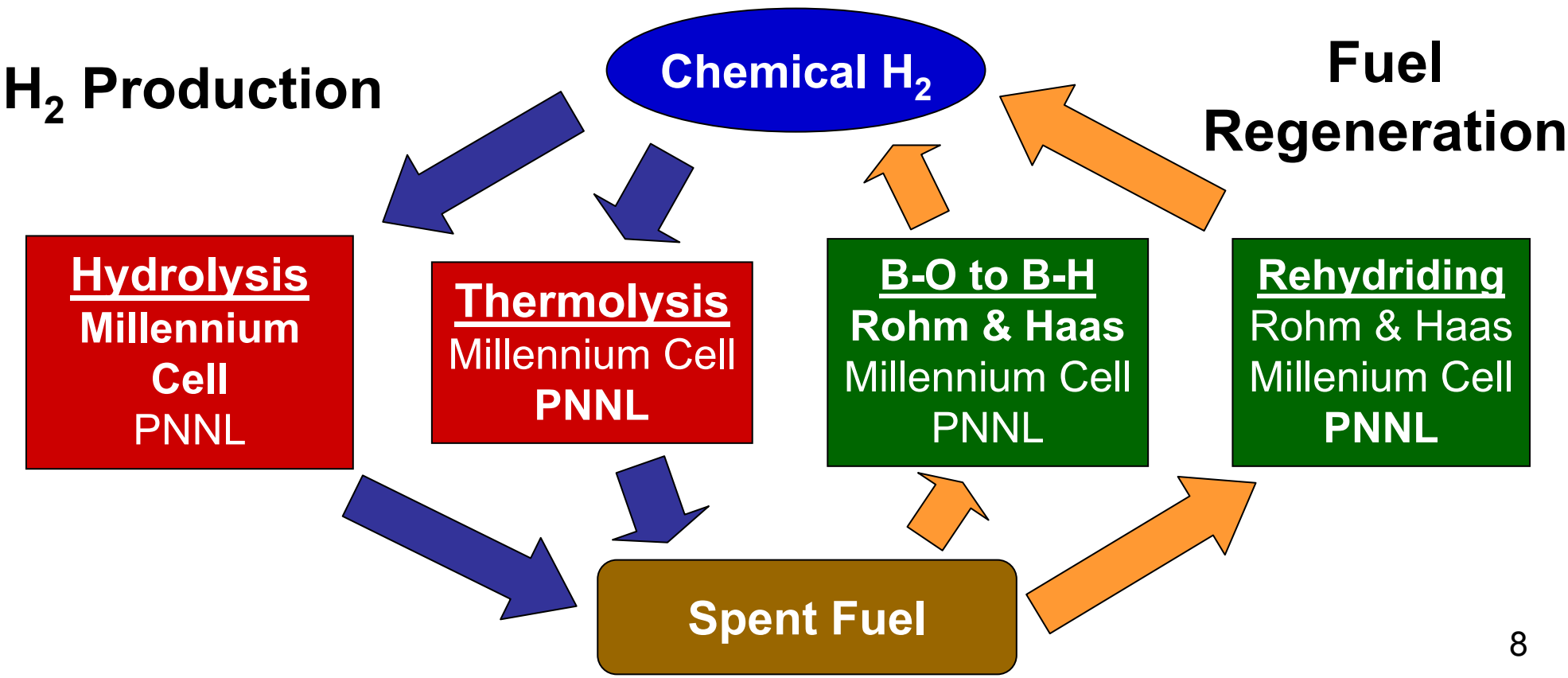
- Tier I: More efficient regeneration of B-H
  - Data mining and brainstorming with Center partners on new energy efficient routes to B-H from B-O
  - Bench scale validation of B-H regeneration approaches in cooperation with LANL, Millennium Cell, and Rohm & Haas
  - Working with Millennium Cell on improved system designs for hydrolysis driven hydrogen production including heat integration and reactor design
  - Assist Rohm & Haas as needed with B-H regeneration engineering
- Tier II: Higher storage density via B-N compounds
  - Help UCLA with computational and thermochemistry support on complex borane hydrolysis and thermolysis
  - Investigation of ammonia borane compounds
    - Computational and experimental approaches
    - Thermochemistry, kinetics, catalysts, scaffold control
      - Interface with LANL & UW on B-N dehydrogenation catalysis

Approach

- Tier II: Continued
  - Regeneration of B-N compounds
    - Computational and experimental investigation of ammonia borane regeneration
    - Flowsheeting for regeneration processes
    - Computational, experimental, and engineering support
  - Engineering of B-N systems
    - Hydrogen generation flowsheeting (solid vs. liquid carriers)
    - Assist LANL & Penn on any engineering needs for their systems
    - Bench scale demonstration of components and process intensification
    - Assessment of on-board requirements and system weight and volume density
    - 1 kg demonstration & life cycle inventory to assess costs, etc.
- Tier III: New hydrogen storage compounds beyond boron
  - Computational screening of new liquid carriers
    - Assess reversibility & density
  - Support UC Davis through computations on Al, N, P materials
  - Support other Center partners within Tier III as needed

Engineering & Analysis Activities

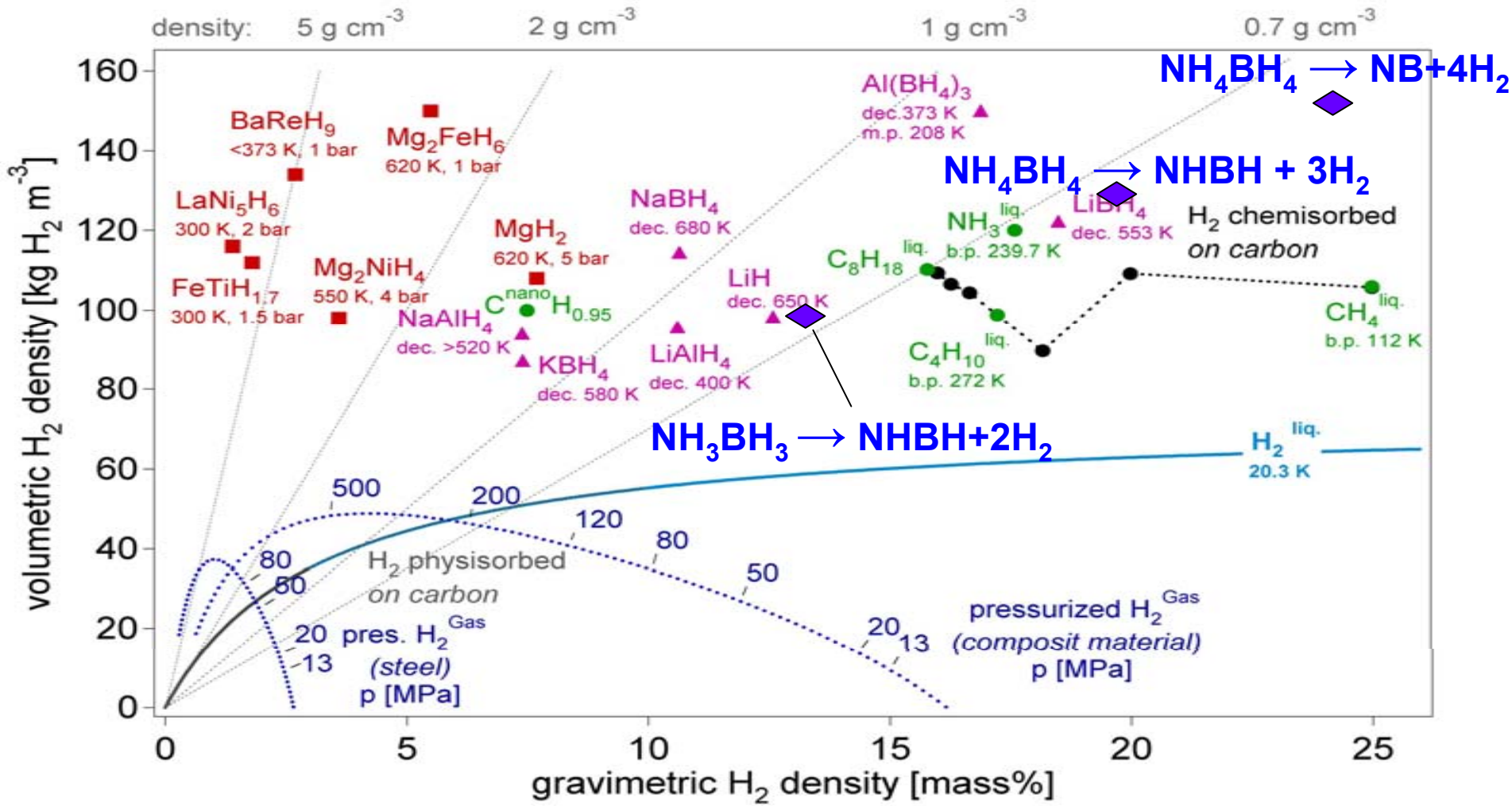
- Regeneration of the fuel likely off-board.
- Engineering aspects of the work are divided into two pieces: production & regeneration.



Technical Accomplishments/ Progress/Results

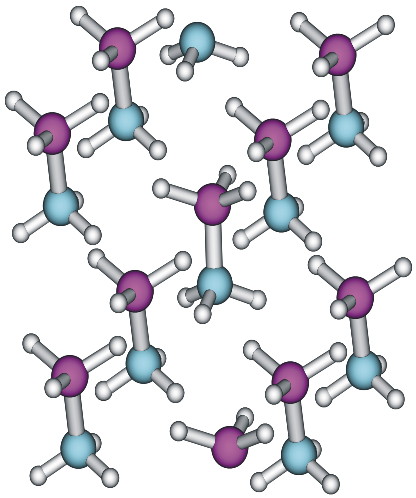
- Center project is a new start, but preliminary results have been obtained largely on ammonia borane.
- Support for this project prior to Center award was through PNNL's Laboratory Directed Research and Development.

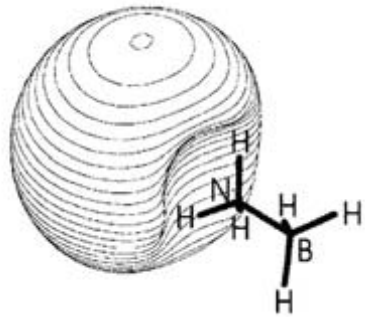
N-B Materials Show Promise for High Density Storage



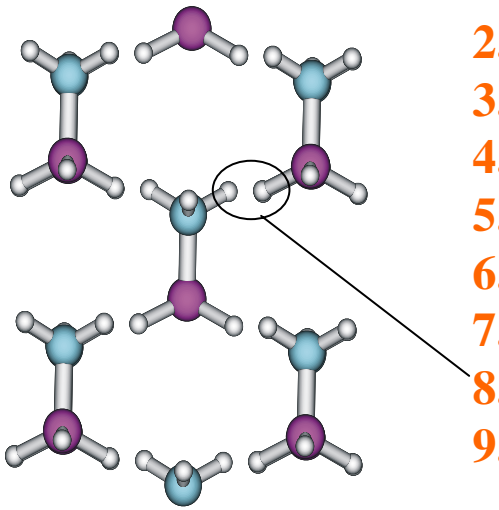
Ref: A. Züttel, “Materials for hydrogen storage”, materials today, Septemper (2003), pp. 18-27

NH_3BH_3 – Computations Show Potentially High Storage Capacity



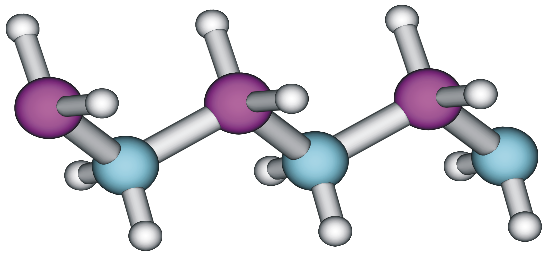


$H_3B \leftarrow :NH_3$ Electron donor-acceptor bond
Large dipole moment of 5.3 D
The H_3B-NH_3 bond energy is 25 kcal/mol



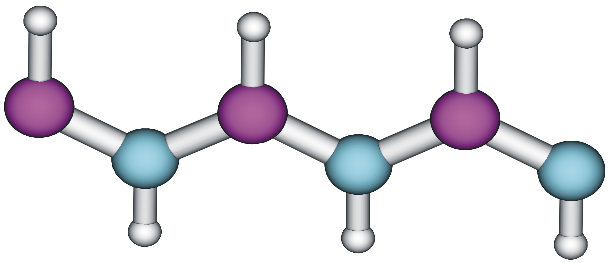
1. **$NH_3BH_3 \rightarrow BN + 3H_2$ 19.5wt% H_2**
2. **$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$ at 110 C and 1 atm.**
3. **First order-disorder phase transition at 225 K**
4. **The low T structure is orthorombic, the high T tetragonal**
5. **$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$; ΔH=8 kcal/mol (calculated)**
6. **Density 0.74 g/cm^3. MP 104.5 C**
7. **The calculated cohesive energy is 16.6 kcal/mol**
8. **Electrostatic bonding between H^+ and H^- (dihydrogen bond)**
9. **NH_3BH_3 is an insulator**

Computations: NH_2BH_2 & NHBH are Polymeric Compounds



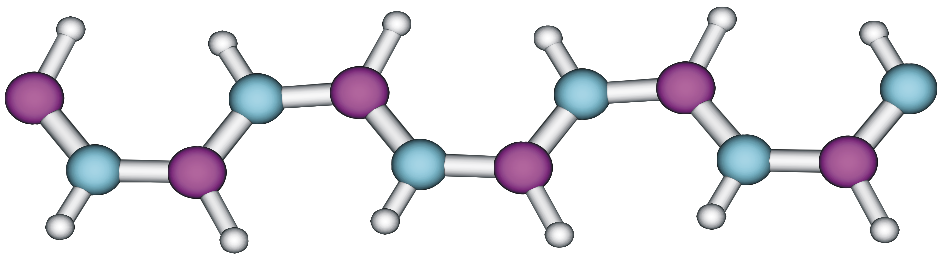
1. NH_2BH_2 is analogous to polyethylene
2. $NH_2BH_2 \rightarrow NHBH + H_2$ at 170 C and 1 atm
3. $NH_2BH_2 \rightarrow NHBH + H_2$; ΔH=-3 kcal/mol (calculated)
4. Undoped NH_2BH_2 is an insulator

All trans NH_2BH_2



trans-NHBH

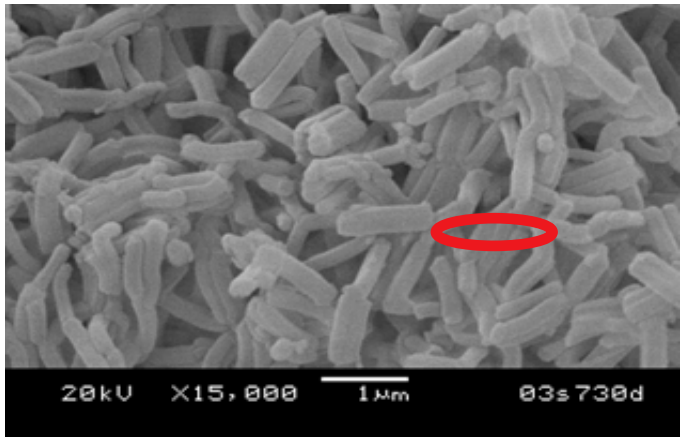
1. NHBH is analogous to polyacetylene
2. $NHBH \rightarrow BN + H_2$ at 500 C and 1 atm
3. $NHBH \rightarrow BN + H_2$; ΔH=-9 kcal/mol (calculated)
4. Undoped NHBH is an insulator

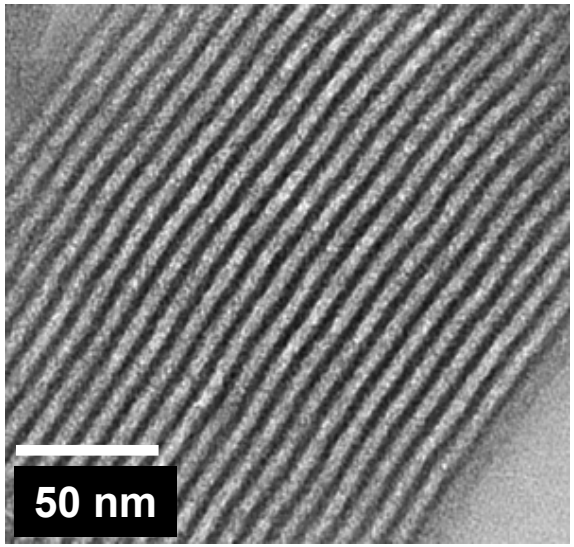


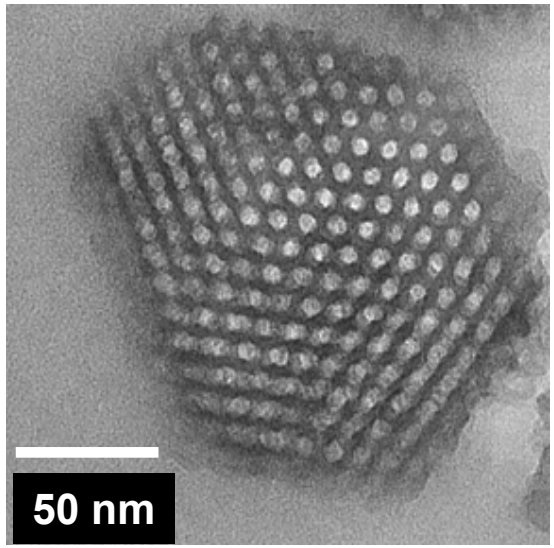
cis-NHBH

Scaffold Supported NH_3BH_3

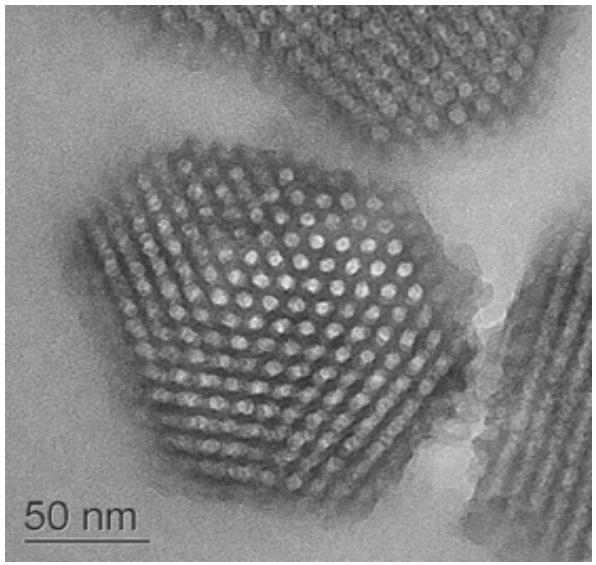
Meso-Porous Substrate SBA-15 (amorphous Silica)





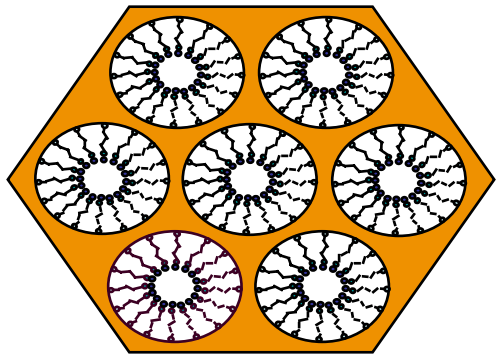


6.5 nm Aligned Pores



NH_3BH_3

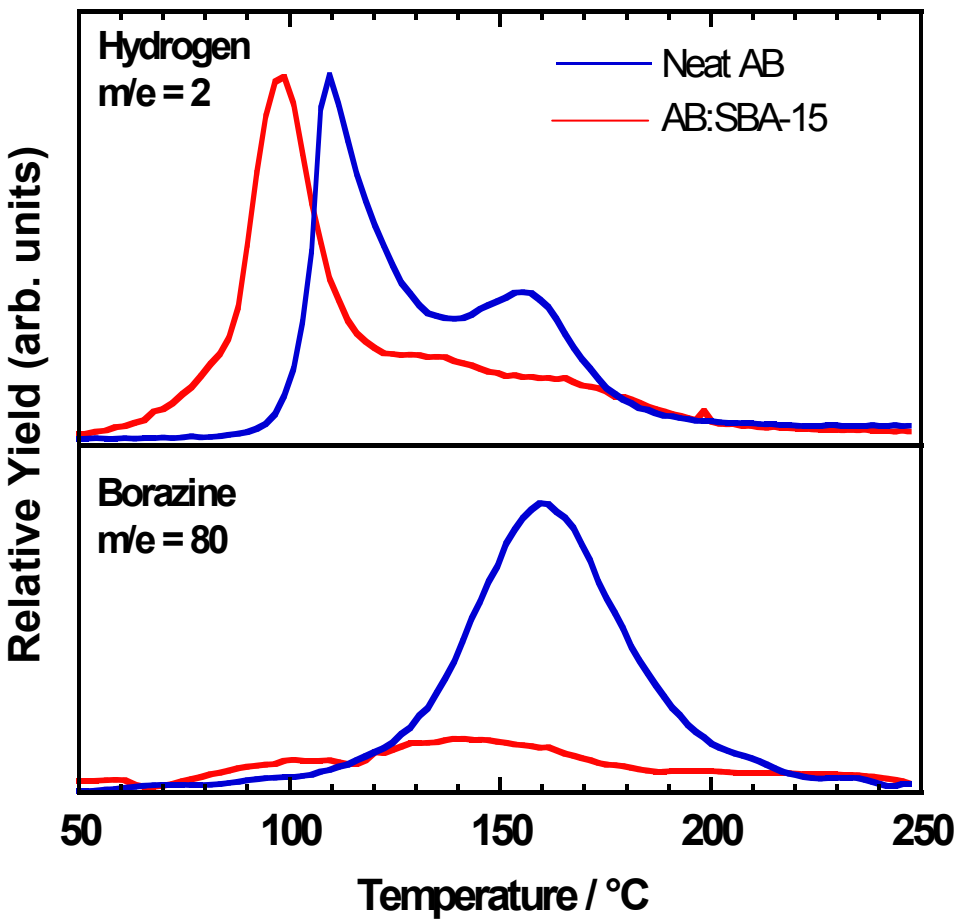
Add saturated ether solution of NH_3BH_3 to SBA-15 (*Incipient wetness*)



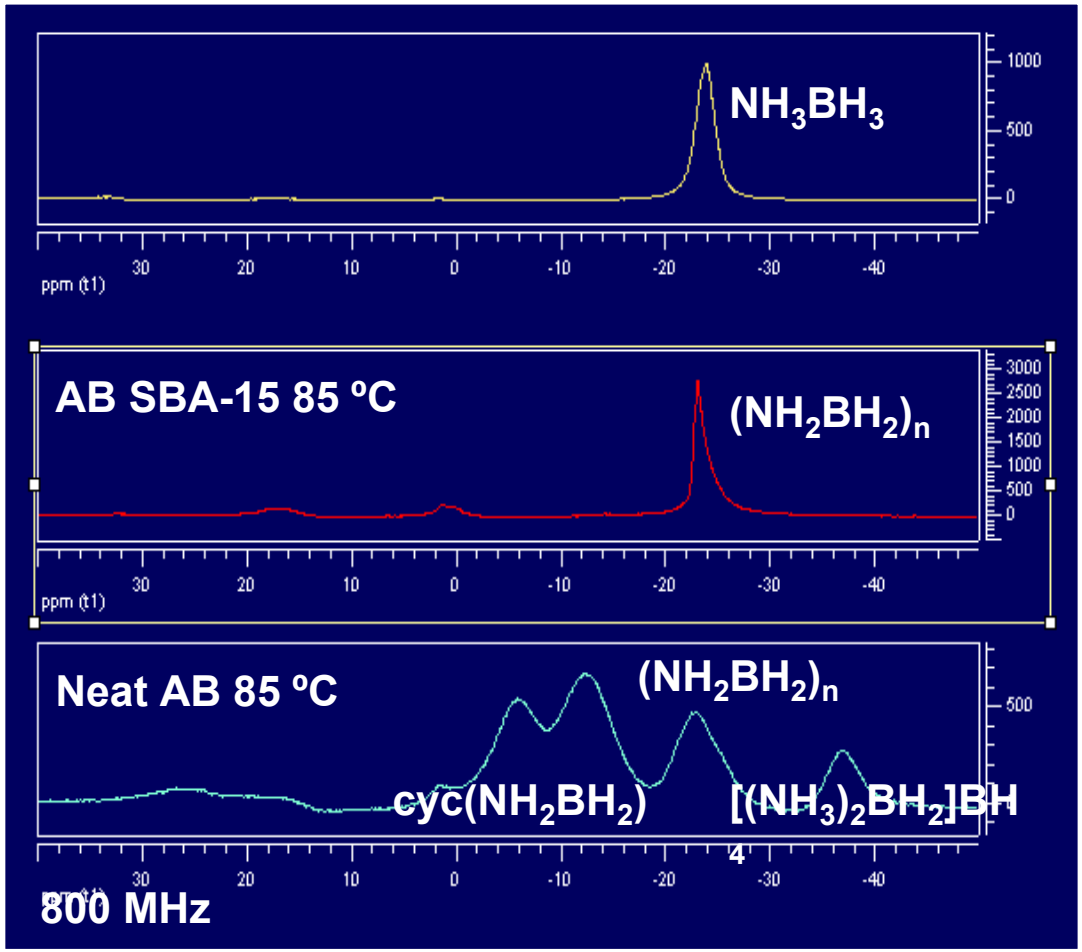
Ammonia borane (AB) infiltrated

Scaffold Support Enhances Hydrogen Purity

TPD-MS products

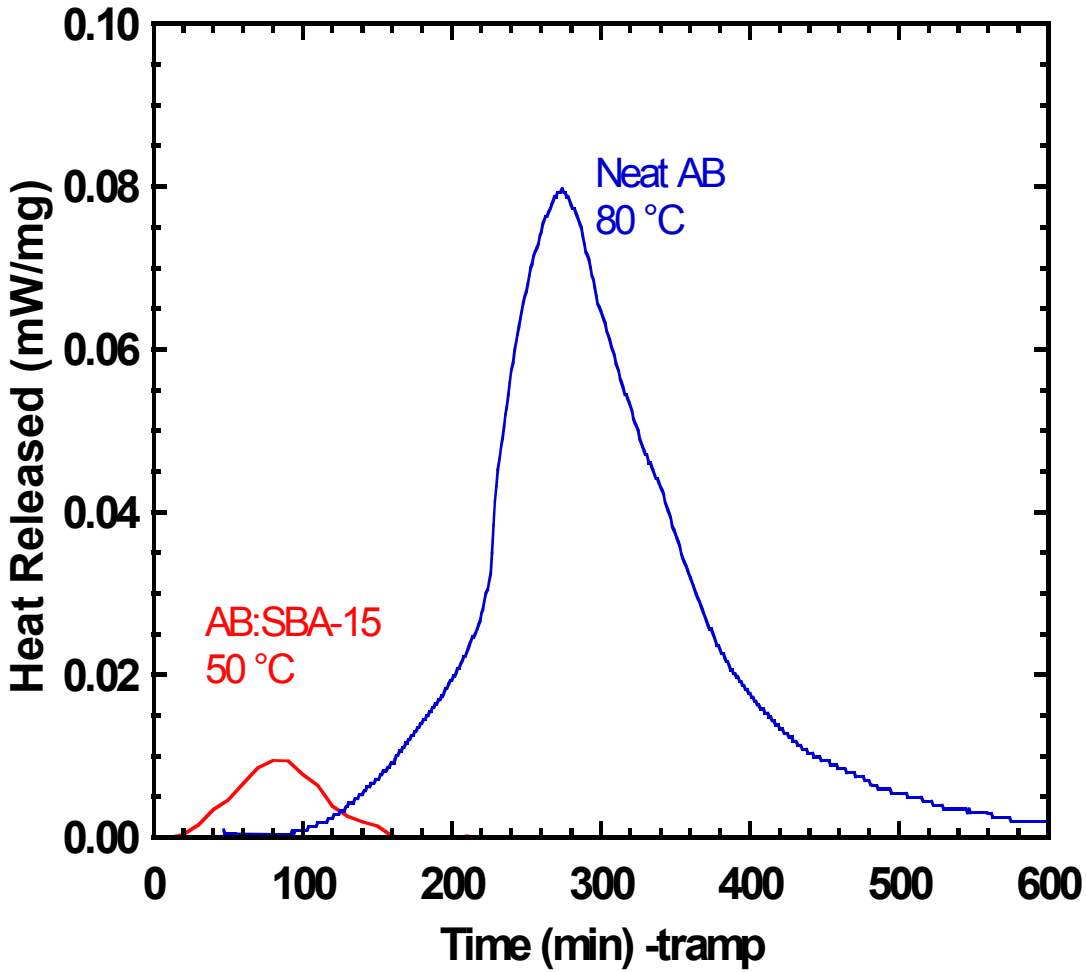


^{11}B NMR products



Thermodynamics: Use of Waste Heat from Fuel Cell Possible

- SBA-15 scaffold allows release of hydrogen at lower temperature
- Hydrogen generated below 100°C on the scaffold material
- Amount of heat released is less than neat material indicating closer to thermoneutral

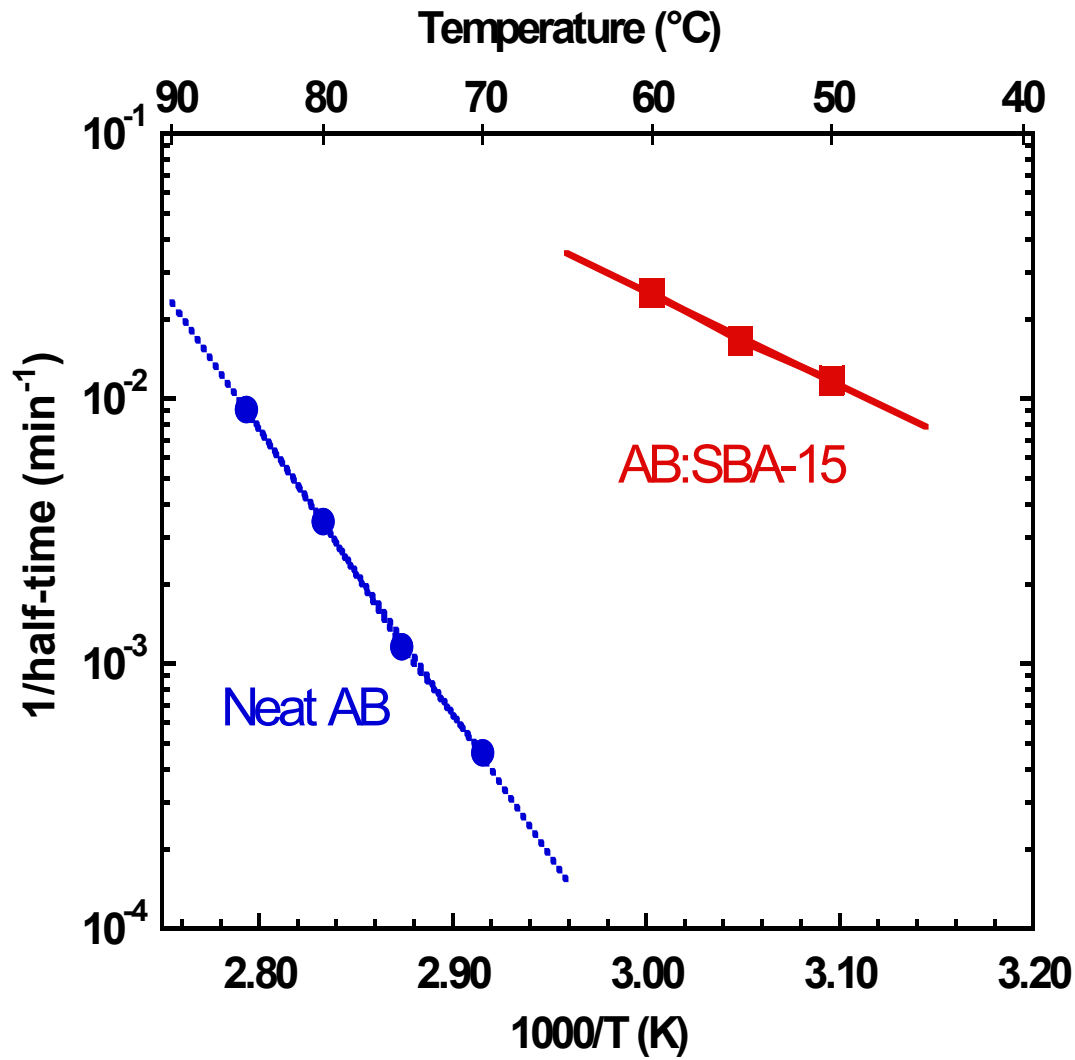


ΔH_{Neat} = -5.1 kcal/mol

$\Delta H_{Scaffold}$ = -0.1 kcal/mol

Kinetics: H_2 Generation Rate is Higher with Scaffold Support

- Arrhenius treatment of the data indicate that hydrogen release is about 100 times faster with the scaffold at 70°C.



Neat: E_a = 44.7 kcal/mol

Scaffold: E_a = 16 kcal/mol

PNNL Milestones for Year 1

• Assemble proprietary resources for data mining	Q2
• Assess preliminary candidate routes from data mining	Q4
• Determine thermodynamic stability of complex boranes (theory)	Q1
• Determine thermodynamic feasibility of BNH hydrogenation (theory)	Q1
• Determine thermodynamics of hydrogenation for BNH	Q4
• Synthesis of scaffolds of varying pore diameter	Q4
• Preliminary identification of B-N-C compounds of greatest promise	Q4
• Heteroatom-organics: determine thermodynamics of hydrogen release (theory)	Q4
• Prepare at least one storage candidate from Tier 3	Q4
• State-of-the-art engineered systems assessed and technical targets defined for core engineering	Q3
• Flowsheets and P&IDs complete for model liquid and solid systems	Q4
• Establish grand challenge project at MSCF ('Computational Design of Materials for Hydrogen Storage' awarded 900,000 node-hours per year for 3 years)	Q1
• Obtain dedicated glove box for center work at PNNL	Q4
• Demonstration and calibration of test equipment for thermochemistry measurements	Q4

Clear path or completed

Issues still being worked

Responses to Previous Year Reviewers' Comments

- New Project: There are no comments to address

Future Work

- Data mining at US Borax and Rohm & Haas libraries
  - Validate viable routes on bench scale
  - Downselection to limited target reactions
- Complex borane hydrolysis: computational and thermochemistry support for UCLA
- Ammonia borane dehydrogenation
  - Determine thermodynamic stability
  - Understand controlling factors

Future Work

- $[BNH]_x$ hydrogenation
  - Determine theoretical ability to hydrogenate
  - Understand thermodynamics of hydrogenation
- Scaffolds
  - Look at the effect of pore diameter on thermodynamics and kinetics
  - Develop theoretical treatments to scaffolding

Future Work

- Heteroatom-containing organics
  - Computational thermodynamics used to screen candidate compounds
  - Prepare at least one candidate and examine on the bench
- Main group hydrides
  - Theoretically evaluate hydrogen storage capabilities of the Al-P systems for UC Davis

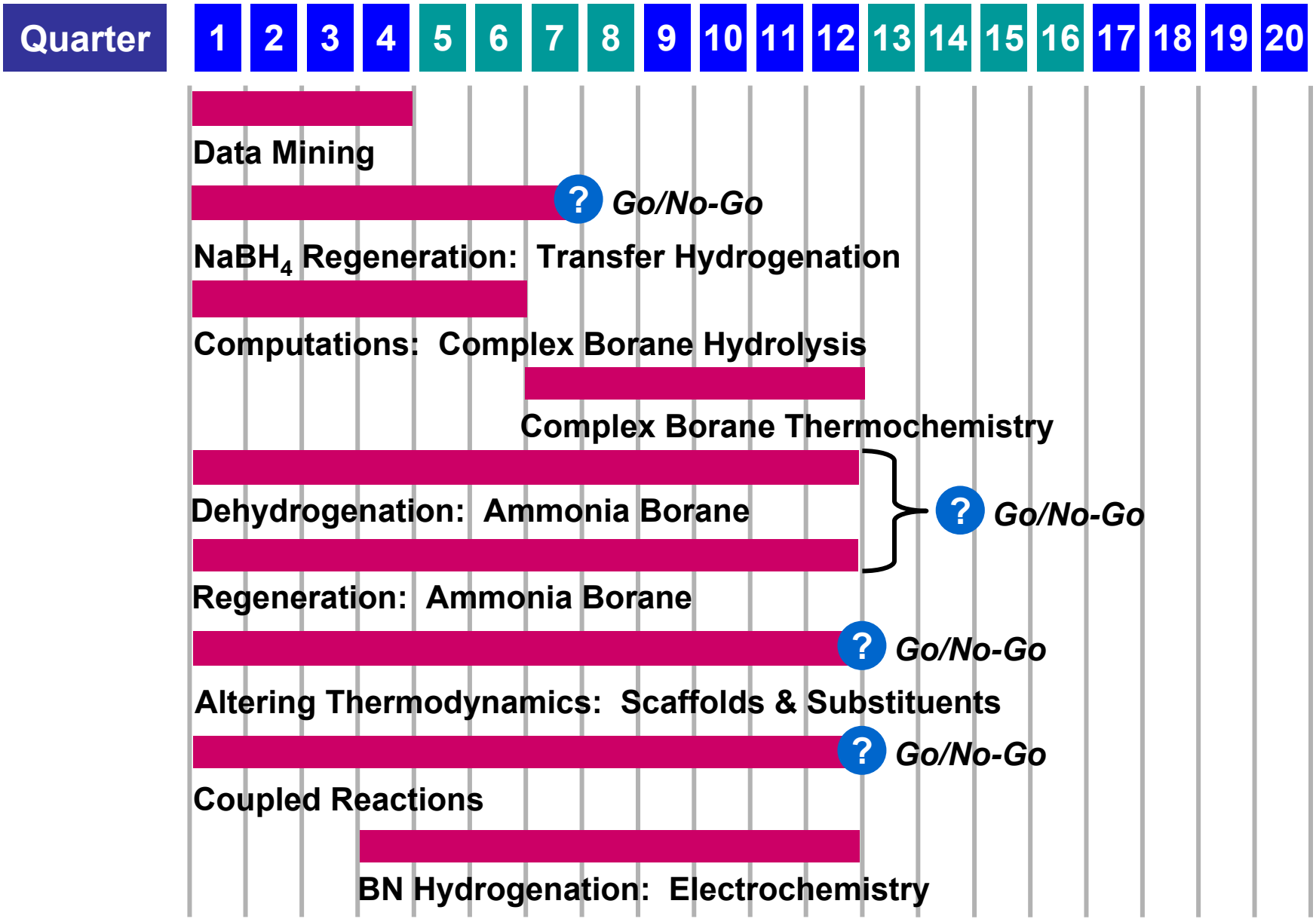
Future Work

- Substituents
  - Use theory and experiment to understand how heteroatoms and functional groups affect thermodynamics
- Complex reactions
  - Identify particular boranes/borohydride/metal hydride and amine combinations (cocktails) that improve thermodynamic parameters for facile regeneration

Future Work

- Engineering
  - Baseline state-of-the-art and define technical targets for on-board systems
  - Flowsheets for thermolysis of solid and liquid carriers
  - Assist Millennium Cell (H_2 generation) and Rohm & Haas (B-H regeneration) as needed on $NaBH_4$ systems

Project Schedule & Decision Points



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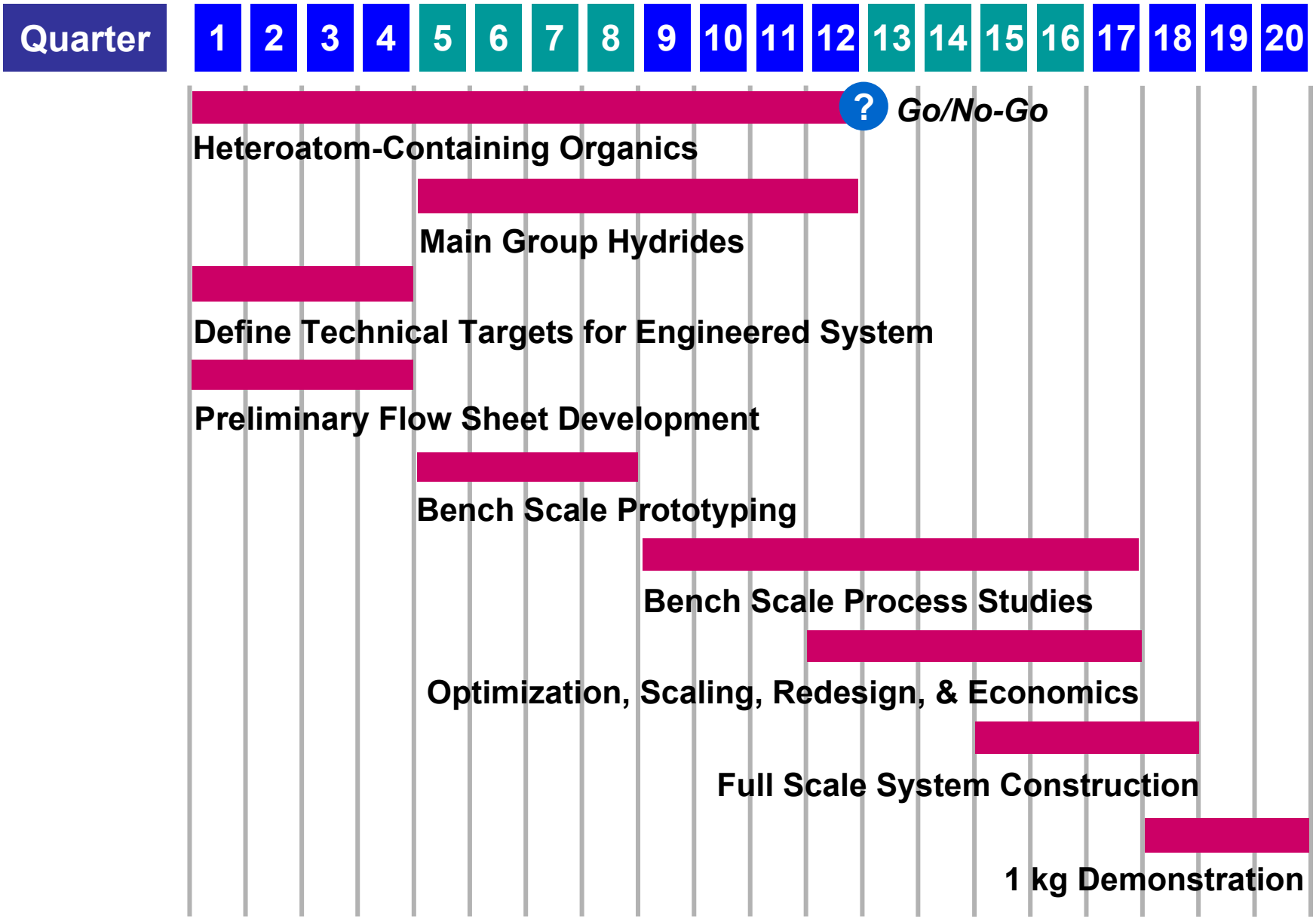
Project Schedule & Decision Points



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Publications and Presentations (since Jan 1, 2005)

- PNNL has been investigating ammonia borane and other compounds for a little over one year. Support for that work will continue under the Center project.
  - “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.
  - “Mechanistic studies of hydrogen formation from amineborane complexes”. R. Scott Smith, Bruce D. Kay, Liyu Li, Nancy Hess, Maciej Gutowski, Benjamin Schmid & Tom Autrey. Presented at the 229th National American Chemical Society Meeting, San Diego, March 2005.
  - "Computational Studies of Materials for Hydrogen Storage. The NBH6 Compounds", M. Gutowski, The Johns Hopkins University, Baltimore, MD, January 20, 2005.
  - "High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems and hydrocarbon fuels", David A Dixon, Maciej Gutowski, Lisa Pollack, Theresa L. Windus, Wibe A. deJong, 229th ACS National Meeting, San Diego, California, March 13-17, 2005.
  - "Theoretical Characterization of the NHxBHx Compounds ", M. Gutowski, 2005 National APS Meeting, Los Angeles, California, March 21-25, 2005.