

2010 Overview and Wrapup

DOE Chemical Hydrogen Storage Center of Excellence

Kevin Ott

Los Alamos National Laboratory

June 10, 2010

Project ST 036



Overview

Timeline

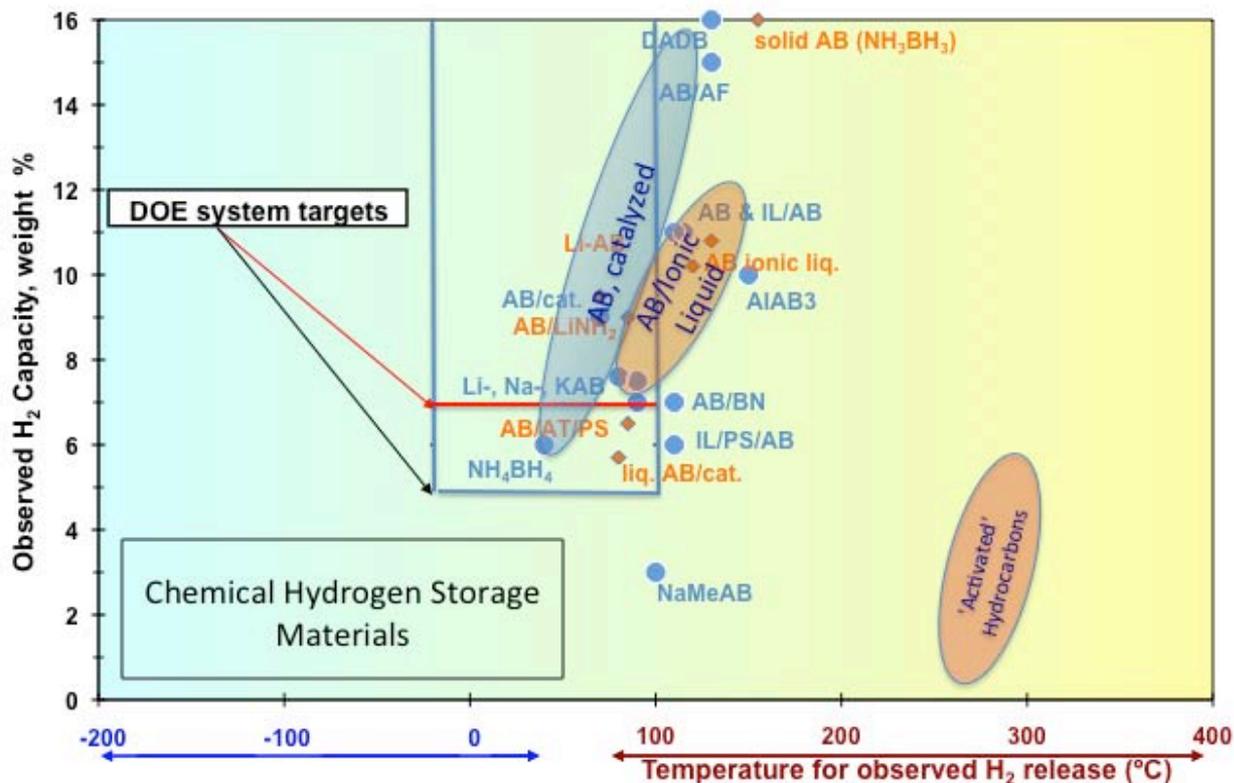
- Start: March 2005
- End: March 2010
- 100% Complete
- Management budget \$400K (PNNL + LANL)

Barriers

- Weight and Volume
- H₂ Flow Rate
- Regeneration Process
- Energy Efficiency
- Cost
- System Life-Cycle Assessments



Amine Boranes and Derivatives – High Capacity Exothermic Materials Enabling Rapid Release of H₂ at Moderate Temp



Amine boranes are one promising class of storage materials

- High H content – up to 16 wt. %
- **Exothermic hydrogen release; enables very high rates of H₂ release**
- **Multiple release strategies:** thermal, catalytic, chemical additives activate AB to release
- Solid and liquid systems
- High H content metal derivatives – the metal amidoboranes, MABs.

Ammonia borane and derivatives have potential to meet DOE system targets for capacity, rates of H₂ release over a range of temperatures appropriate to fuel cell applications

Outline of Historical Overview of CHSCoE

- Objectives and approach of the Center
- How the Center implemented the approach – some history of the evolution of the Center
 - What did and did not succeed – robust down select process for materials
- What the Center accomplished toward meeting the DOE targets
 - **First fill synthesis of NaBH₄ and AB—from the mine to the plant gate**
 - Chemistry for the first fill of ammonia borane using vastly improved chemical and energy efficiencies relative to Schlesinger for synthesis of NaBH₄
 - Resource and demand analysis of borax for AB fuels
 - **Release**
 - Initially, hydrolysis of sodium borohydride and polyhedral boranes to H₂
 - Then, thermolysis and catalytic release of innumerable permutations involving ammonia borane, and its metal amidoborane derivatives
 - Demonstrated capacities and rates with the potential to meet DOE targets; ANL working toward preliminary assessment of onboard release system
 - **Regeneration of spent fuel**
 - In the short history of the Center, we have demonstrated 7 complete regeneration cycles; one cost estimate finalized, one in process
 - The regeneration of spent fuel has evolved from rather high complexity to great simplicity

Objectives and Approach – final year of Center

Conceive, research, develop and validate advanced on-board chemical hydrogen storage materials with the potential to overcome technical barriers and meet 2010 with potential to meet 2015 DOE system goals:

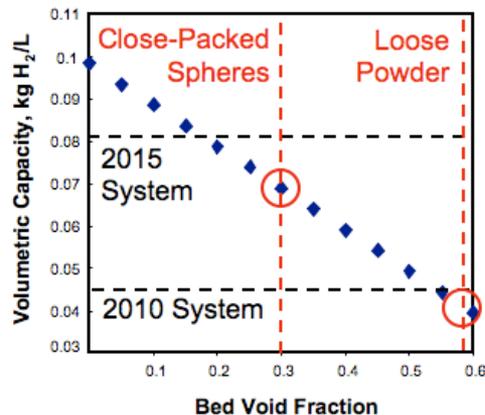
- **Regenerate** spent fuel by demonstrating energy and cost efficient chemical processes leading to off board regeneration of fuel
- **Assess** materials and processes using engineering analysis and studies using DOE targets as guidance in order to:
- **Down select** chemistries, materials, catalysts to control thermochemistry and reaction pathways for optimal hydrogen release
- **Analyze life cycle** issues: boron resources, first fill and spent fuel regeneration costs
- **Make recommendations** to DOE of most promising chemical systems for more detailed work and engineering development in Final Reports to DOE
- **Transfer information** and prioritization of chemical hydrogen storage materials and processes to the Hydrogen Storage Engineering Center for analysis and development of systems

Approach: Theory & Modeling Have Given Expert Guidance to All Center Experimental Efforts

- Regeneration
 - Computation of thermodynamic properties of reactants, intermediates, and products and pathways
 - Computation/calibration of physical properties of intermediates for input into R&H/Dow cost analyses
- Hydrogen Release
 - Calculation of energetics of dehydrogenation reaction pathways
- New Materials
 - Heats of formation and reaction enthalpies for cyclo-CBN compounds guides synthesis
 - Thermochemistry of metal amidoboranes tests hypotheses for release and direct rehydrogenation

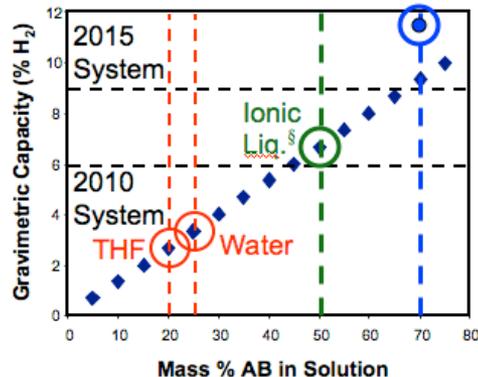
Approach: Engineering Assessments have Guided Center's Research

2 Equiv. H₂ from AB (13.1 wt%)



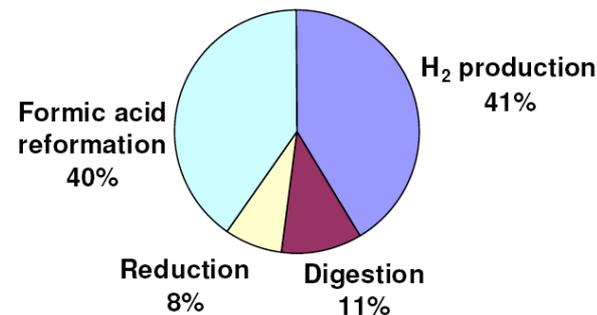
Bed void volume limits capacity to meet targets

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy



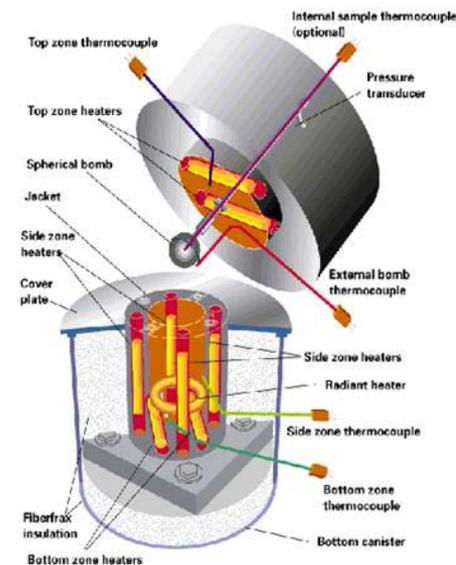
Solvents limit capacity to meet targets

Primary Energy Distribution



Accelerated rate calorimeter used to define solid AB fuel stability from number of vendors

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy



Center's approach guided by insights from engineering requirements was always focused on striving to meet DOE targets

Approach: Partnership in Analysis, Theory Enabled Rapid Experimental Progress in Regeneration

- Dow - Lead Institution
 - Worked with regen team to develop process flow sheets, prioritize expt'l data needs, perform analysis
- Penn, LANL, PNNL
 - Devised and demonstrated chemical regeneration steps and complete cycles. Worked with Dow to define process, develop flow sheets
- Alabama
 - Guided pathway selection using state-of-the-art theoretical techniques, and filled gaps in knowledge of physical properties of intermediates through computational approaches
- TIAX, ANL
 - Independent analysis and validation of Center's efforts



Coordination, Collaboration, and Communication Have Always Been Hallmarks of Our Center

- **Most valuable feature of our early Center concept -- IP agreement that allowed free exchange of ideas and materials among Center partners from the very beginning**
- IP agreement enabled --
 - Regular conference calls and meetings, frequent one-on-one phone calls, site visits to exchange information in real time, develop plans
 - Face-to-face brainstorming meetings (2-3/yr)
- Open conversation enabled coordinated and constant downselection to most promising materials and processes
- Actively participated in Storage Systems Analysis Working Group: cross-Center engineering issues
- **LANL and PNNL partners in Engineering Center of Excellence – input from materials development**

CHSCoE Partners Led or Participated in International Storage Efforts

- LANL initiated regular hydrogen storage and fuel cell meetings with Japanese researchers
 - 6 LANL – NEDO/AIST workshops in Japan and the US
 - Plans to continue
- LANL initiated MOUs and joint research, staff exchange with AIST/Tsukuba (Dr. Akiba) and Hiroshima University (Prof. Kojima)
- PNNL initiated IPHE project with international partners focused on metalamidoboranes
 - Significant participation by LANL
- Coordinated technical personnel exchange and international collaboration
 - PNNL and LANL staff to Japan, summer 2008
 - PNNL staff to China 2009
 - Students from academic partner's labs working alongside National Lab staff
- PNNL and LANL participation in IEA Task 22
- LANL - University of Ottawa – maintained Tom Baker's expertise in catalysis and synthesis of liquid fuels within Center

A recap of how the Center began

- Key approach was to **identify failures fast**, down select, and move on
- Developed early an ‘engineering guided’ downselect process for hydrogen release materials
- Early on, used a ‘life cycle inventory’ approach to assess regeneration and first fill synthesis schemes
- **Started with a three-tiered materials approach**
 - Tier 1: Materials that were more well-developed or ongoing**
 - Tier 2: Materials/processes that avoided B-O bond formation**
 - Tier 3: ‘Beyond Boron’ – approaches for release from activated organics; coupled endo/exothermic reactions to drive release**

The Original Makeup of the Center 2005

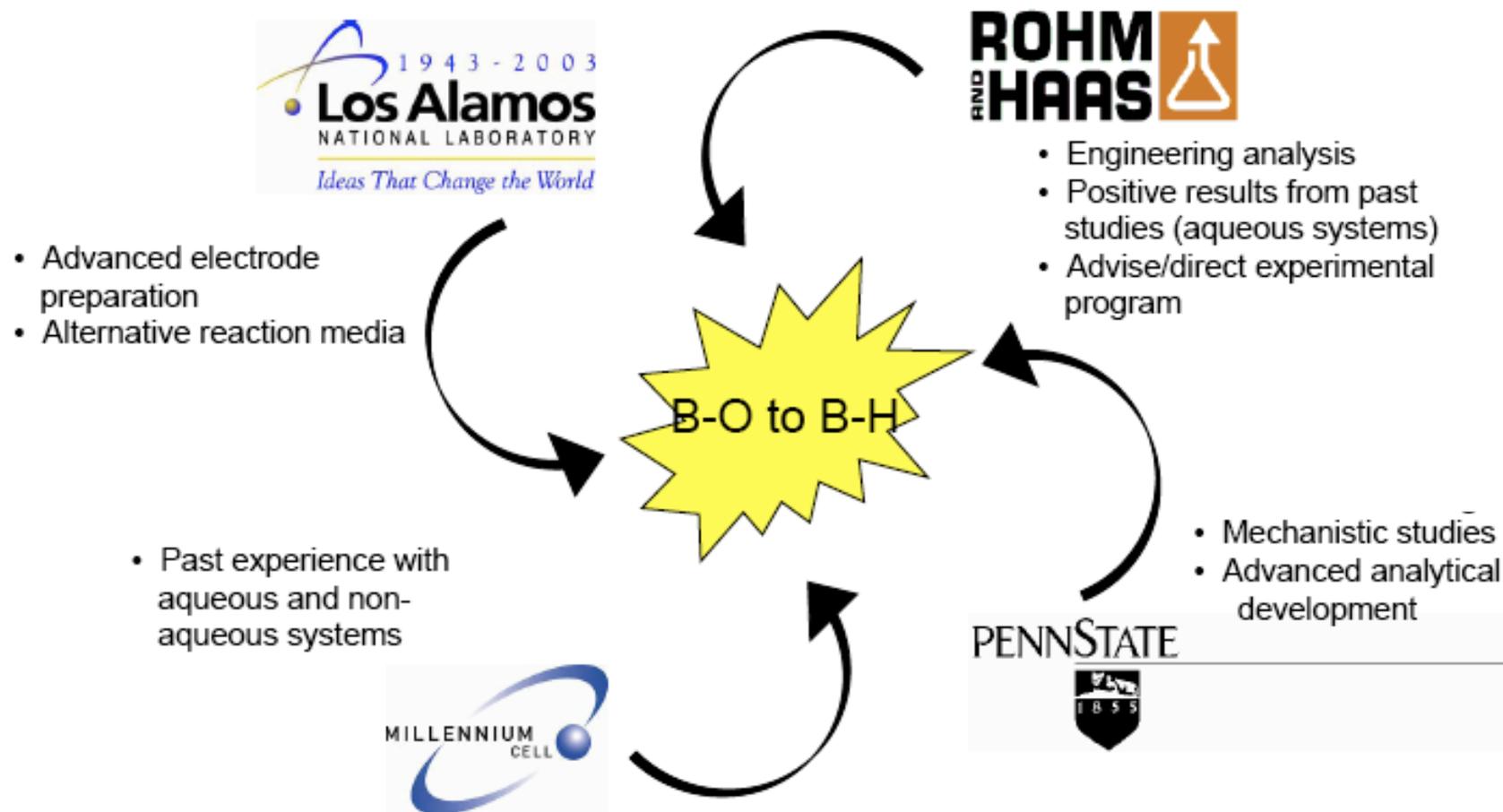


CHSCoE 2010



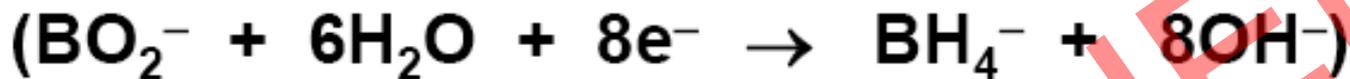
Tier 1 2005: Hydrolysis – regeneration from borates an early concern

Electrochemical Reduction of Borates



Tier 1 2005 Hydrolysis – regeneration from borates an early concern

Electrochemical Reduction of Borates



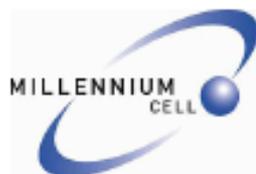
- Engineering analysis
- Positive results from past studies (aqueous systems)
- Advise/direct experimental program

- Advanced electrode preparation
- Alternative reaction media

- Past experience with aqueous and non-aqueous systems

- Mechanistic studies
- Advanced analytical development

B-O to B-H

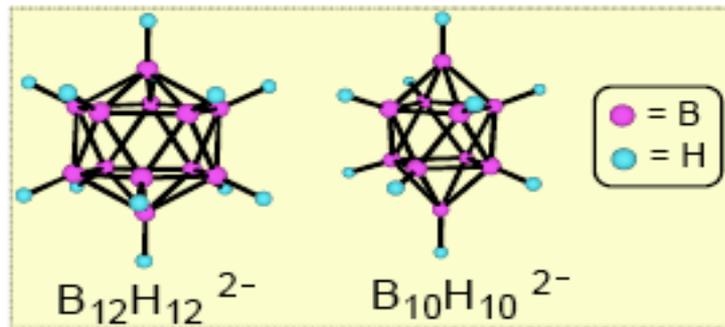


2007 No Go Decision on SBH

2005 Tier 1: Hydrolysis of Polyhedral Boranes – requires borate regeneration

Polyhedral boranes are more stable than borohydride and multiple electron sources

Objective: Optimize catalysts for hydrolysis of polyhedral borane anions using rapid throughput heterogeneous catalyst synthesis and testing



Material storage capacity 9.4 wt% hydrogen (including water)

Future Work:

Thermodynamics, theory and calorimetry

Other H_2 generation routes

- Aminolysis
- Electrochemistry

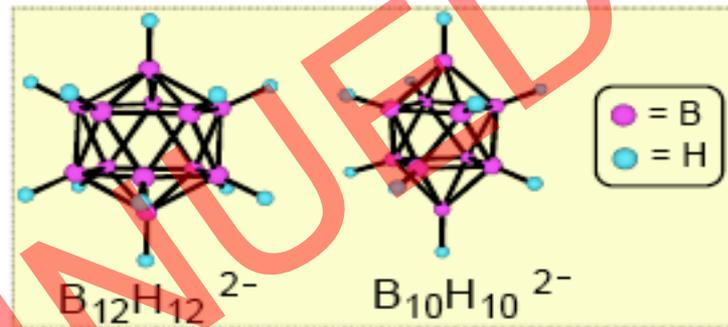
New regeneration routes from borate

UCLA, Intematix,
PNNL, LANL Posters

2005 Tier 1: Hydrolysis of Polyhedral Boranes – requires borate regeneration

Polyhedral boranes are more stable than borohydride and multiple electron sources

Objective: Optimize catalysts for hydrolysis of polyhedral borane anions using rapid throughput heterogeneous catalyst synthesis and testing



Material storage capacity 9.4 wt% hydrogen (including water)

Future Work:

Thermodynamics, theory and calorimetry

Other H_2 generation routes

- Aminolysis
- Electrochemistry

New regeneration routes from borate

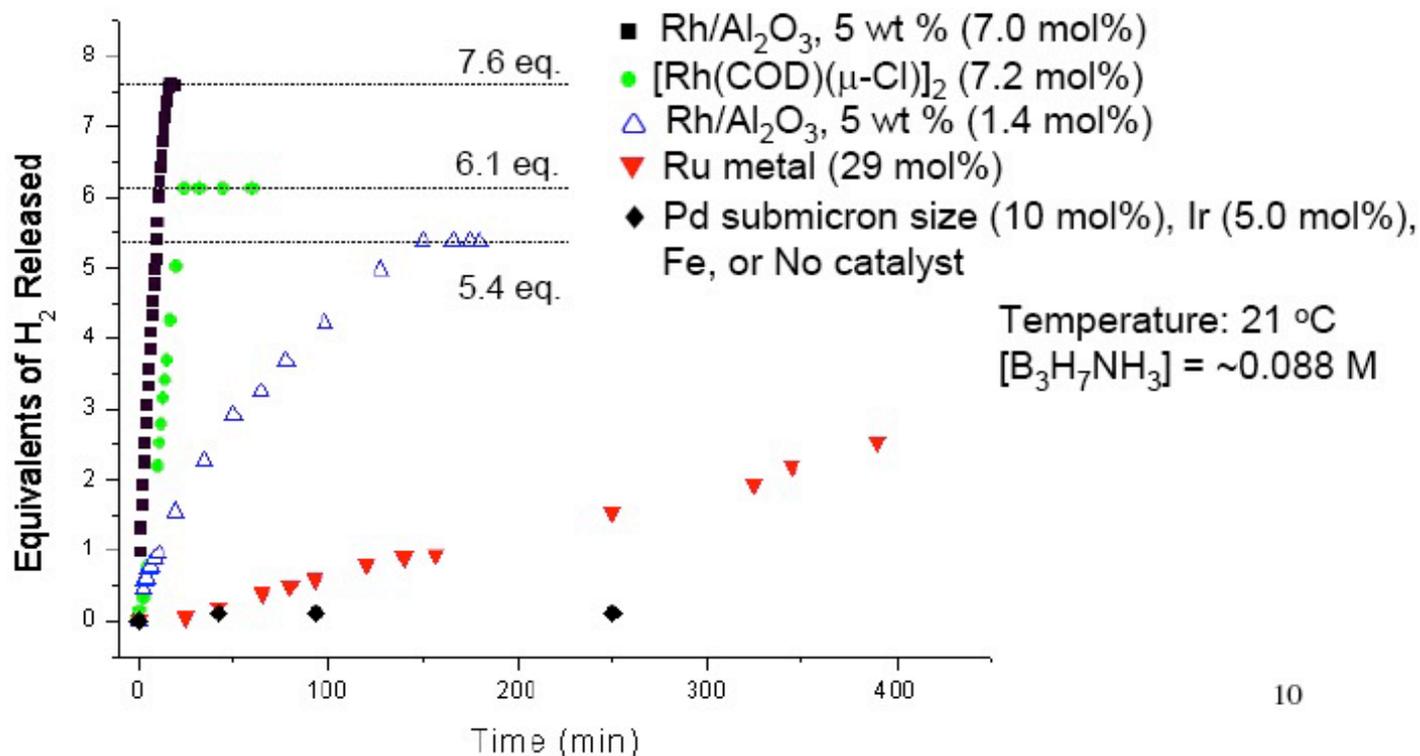
UCLA, Intematix,
PNNL, LANL Posters

2007 No Go Decision on SBH

2005: Penn Discovers Rapid Release from Ammonia Triborane



Metals Catalyze Hydrolysis of $B_3H_7NH_3$

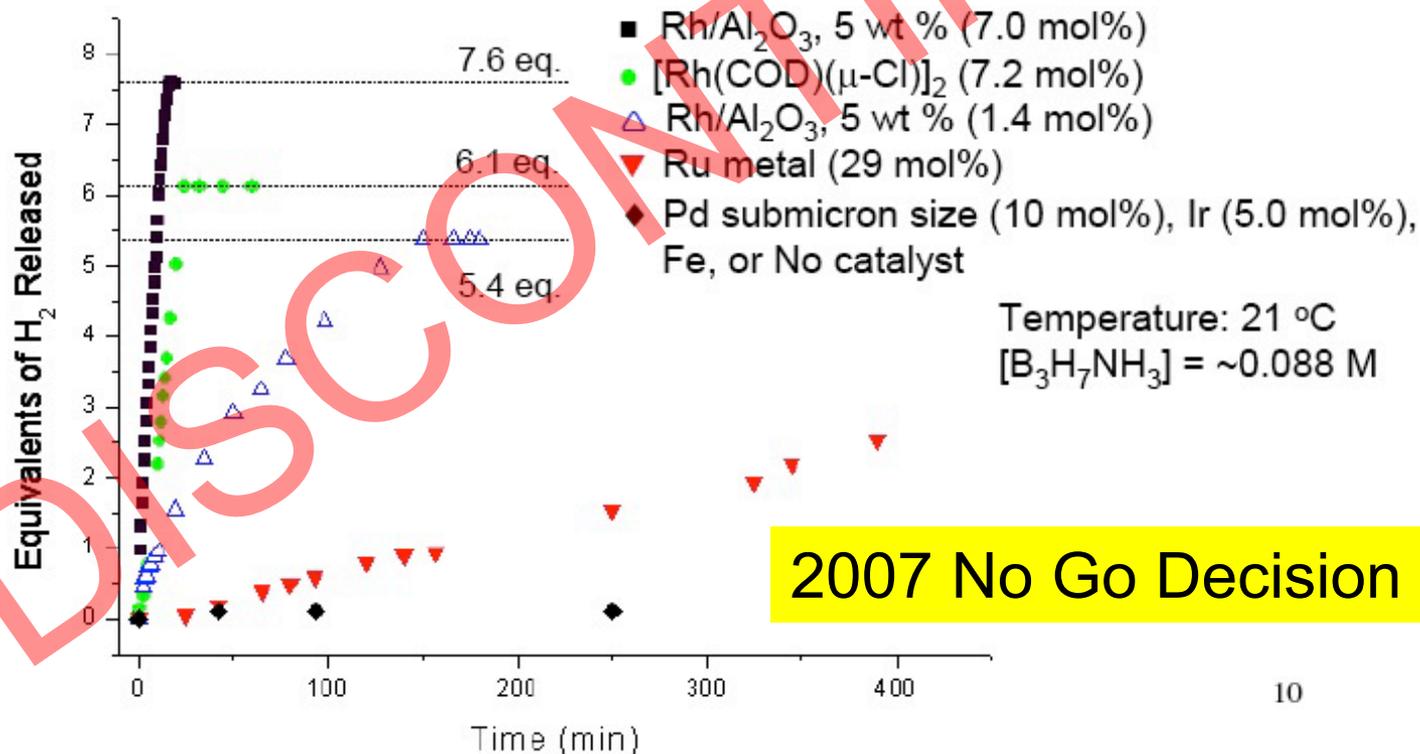


10

2005: Penn Discovers Rapid Release from Ammonia Triborane

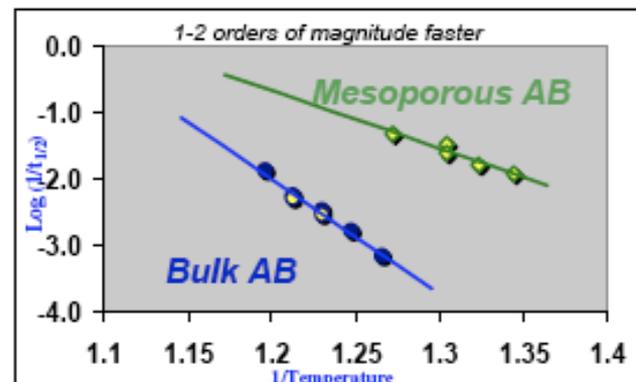
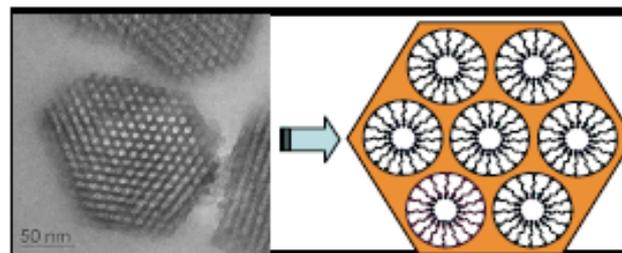
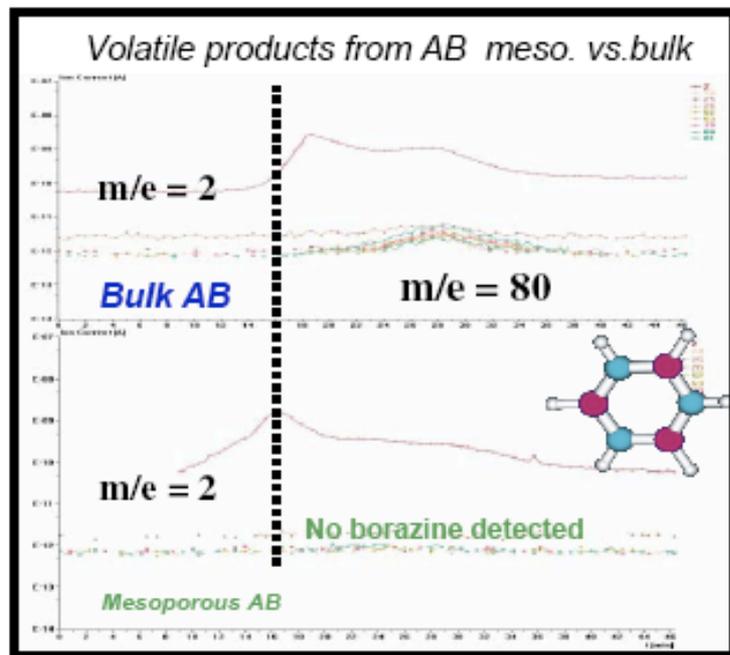
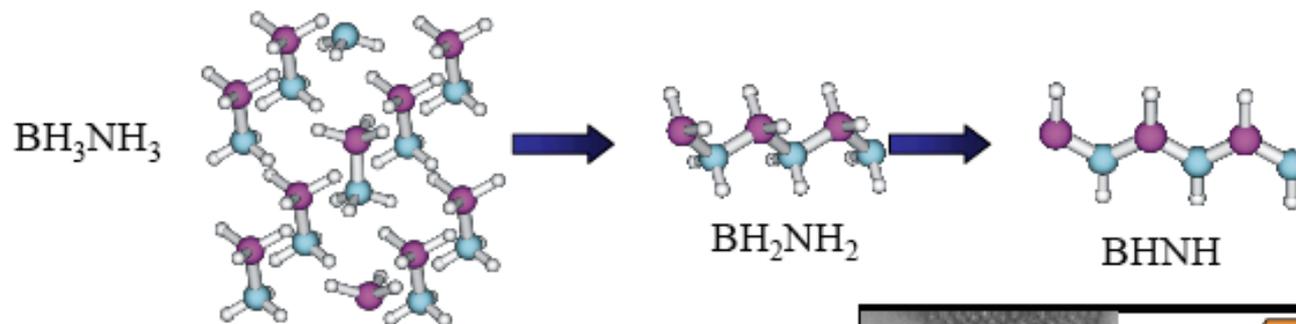


Metals Catalyze Hydrolysis of $B_3H_7NH_3$



2007 No Go Decision on SBH

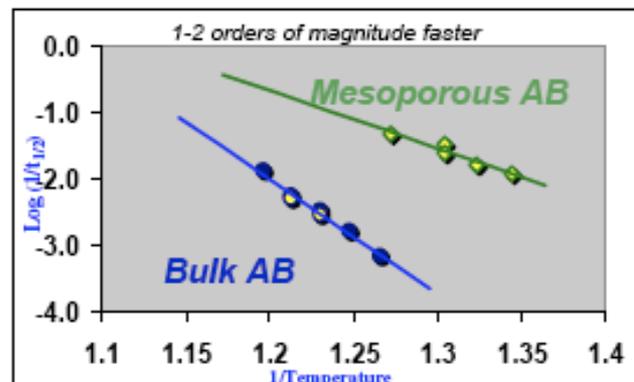
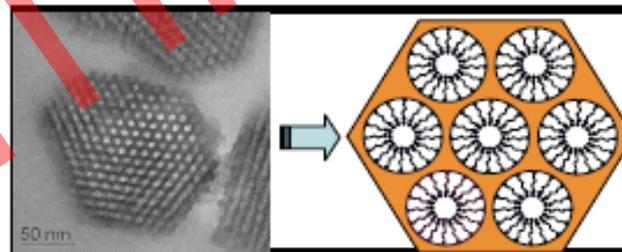
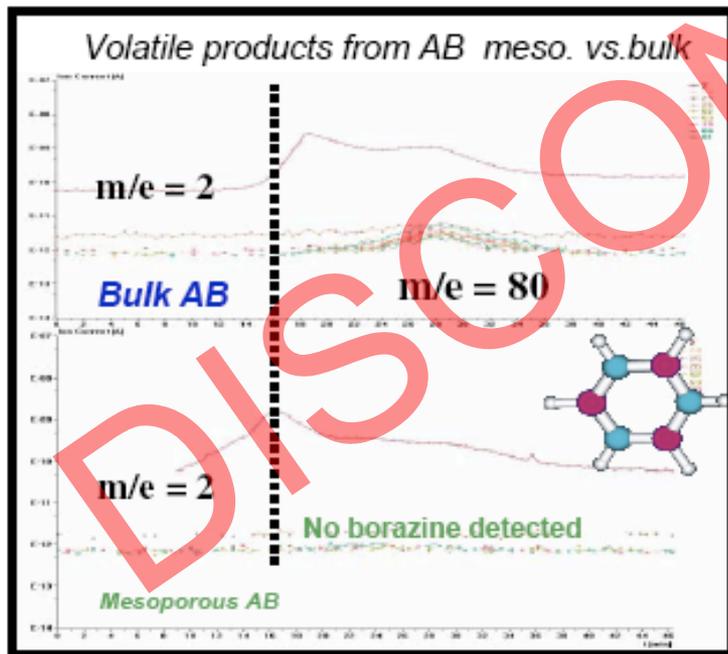
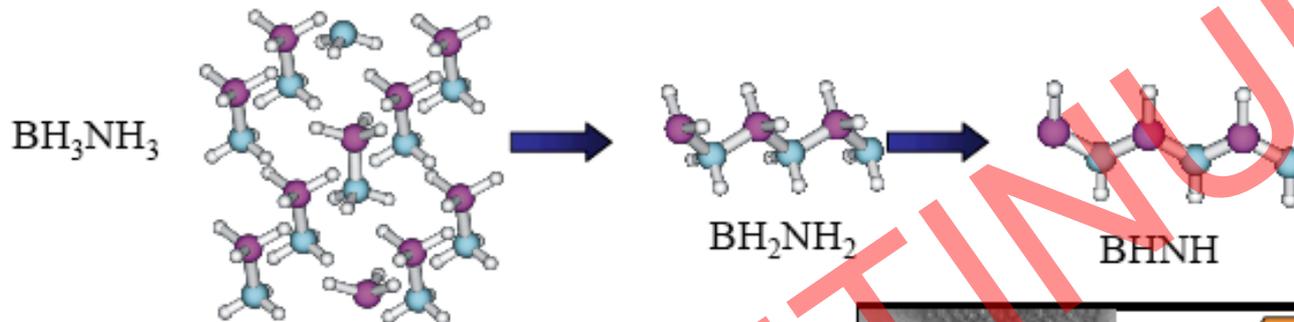
2005 Tier 2: Initially, we knew little of ammonia borane other than it's high potential H₂ capacity



Chemical Hydrogen Storage Center

PNNL Poster 2005

2005 Tier 2: Initially, we knew little of ammonia borane other than it's high potential H₂ capacity

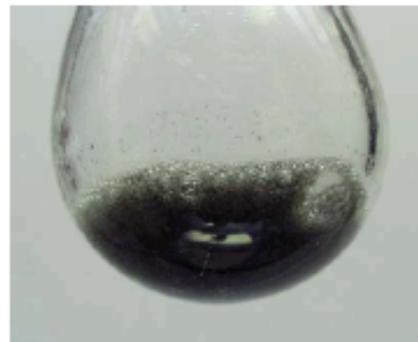
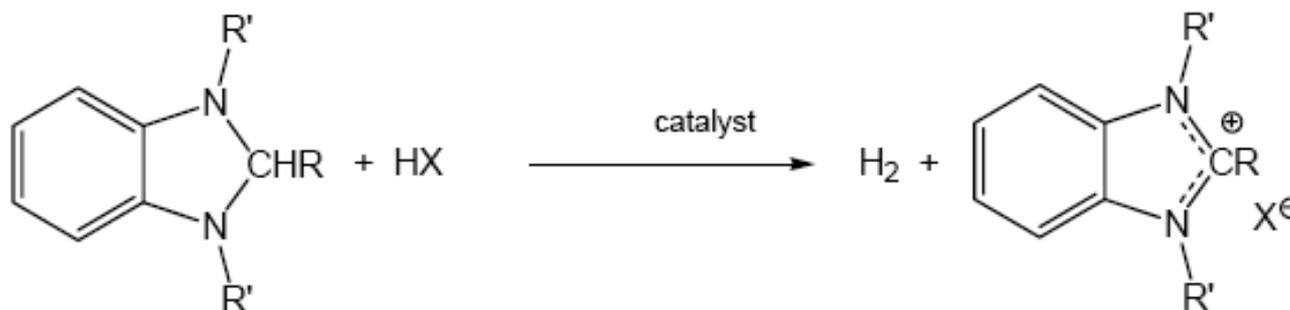


Chemical Hydrogen Storage Center

Gravimetric Penalty of Scaffold

Tier 3: 'Beyond Boron' – activated C-H compounds

Exergonic H₂ Evolution at Ambient Temperature: A Chemical Hydride

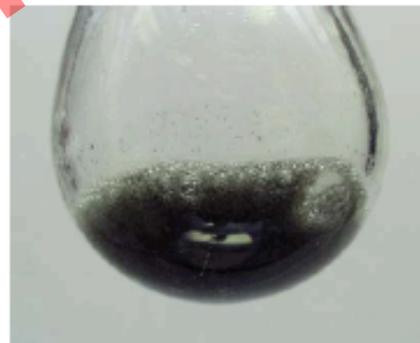
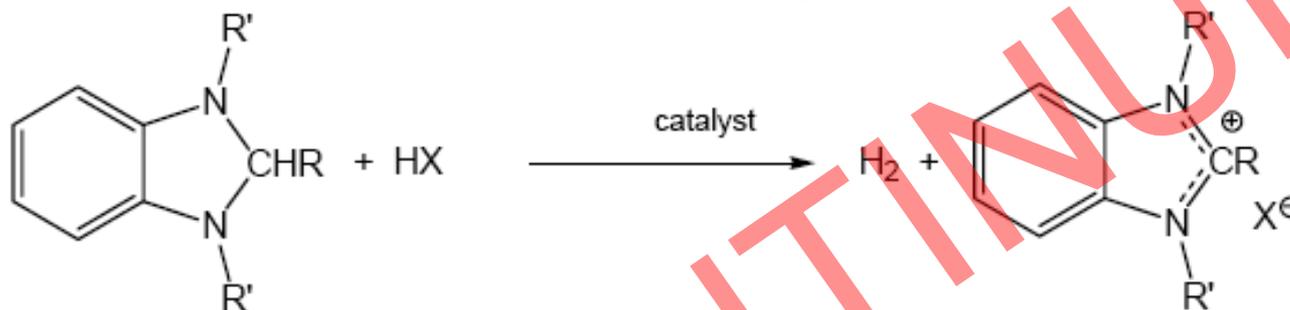


- Demonstration of judicious heteroatom substitution
- Future work to focus on
 - Improving wt% H₂ in related and other systems
 - Increasing rate of H₂ evolution
 - Regeneration

LANL

Tier 3: 'Beyond Boron' – activated C-H compounds

Exergonic H₂ Evolution at Ambient Temperature: A Chemical Hydride



- Demonstration of judicious heteroatom substitution
- Future work to focus on
 - Improving wt% H₂ in related and other systems
 - Increasing rate of H₂ evolution

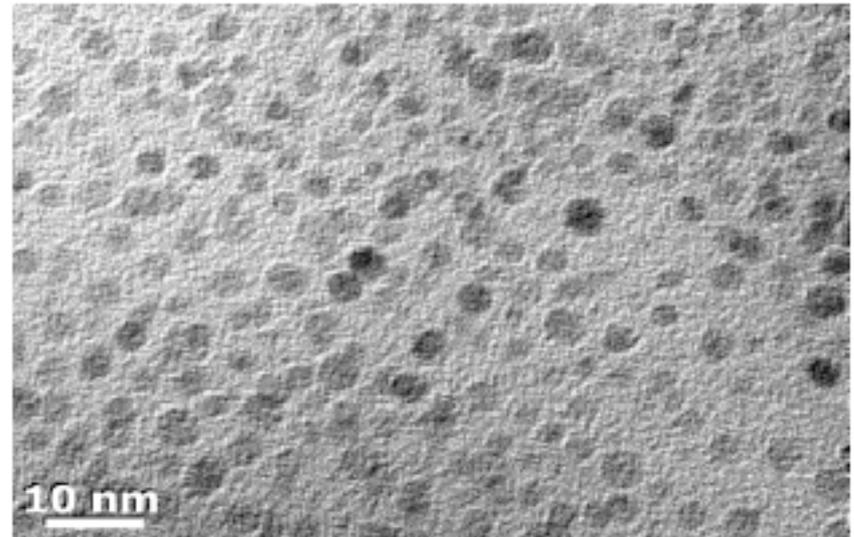
No path to increasing gravimetric capacity

LANL

2005 Tier 3: Nanoparticles for Storage

- Realize the potential to store and release hydrogen
 - Doped-B, Si nanoparticles by solution core-shell synthesis
 - Metal-based nanoparticles by gas-solid synthesis
 - Targets: 1-2 nm particles, compositions
 - $M_{1.0}H_{1.0}$, $M_{1.0}(NH_2)_{1.0}$, $M_{1-x}M'_xH_{1.0}$, $M_{1-x}M'_x(NH_2)_{1.0}$
(M, M' = B, Al, Si, C)
 - Establish ability to hydrogenate, dehydrogenate

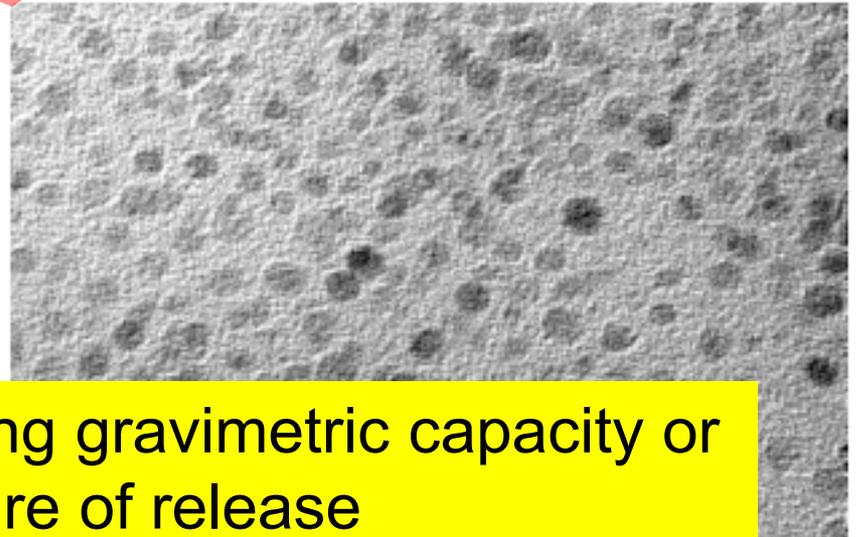
Capped Si nanoparticles
obtained by oxidation of Mg_2Si



2005 Tier 3: Nanoparticles for Storage

- Realize the potential to store and release hydrogen
 - Doped-B, Si nanoparticles by solution core-shell synthesis
 - Metal-based nanoparticles by gas-solid synthesis
 - Targets: 1-2 nm particles, compositions
 - $M_{1.0}H_{1.0}$, $M_{1.0}(NH_2)_{1.0}$, $M_{1-x}M'_xH_{1.0}$, $M_{1-x}M'_x(NH_2)_{1.0}$
(M, M' = B, Al, Si, C)
 - Establish ability to hydrogenate, dehydrogenate

Capped Si nanoparticles
obtained by oxidation of Mg_2Si

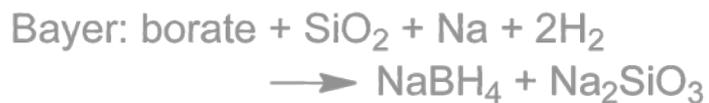
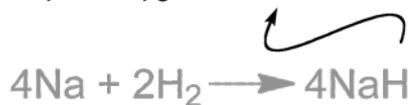


No path to increasing gravimetric capacity or reducing temperature of release

2005 Synthesis of NaBH₄: Existing Routes

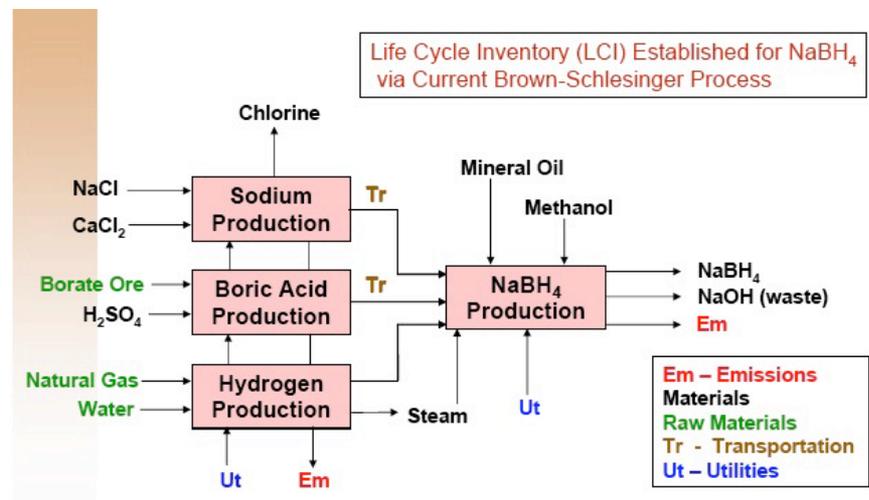
Energy Intensive

- Schlesinger/Brown**



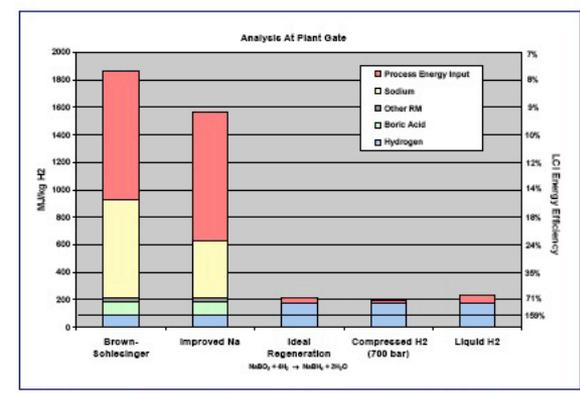
Variants as O acceptors, e.g. Mg/MgO

Metal Reductants Energetically Costly – Minimize or Avoid



ROHM HAARS Life cycle analysis addresses technical barrier: Lack of understanding of environmental impacts (energy usage and emissions) of the generation process 15

Comparison of LCI Gross Energy for H₂ at Regeneration Plant Fenceline



Ideal Regeneration, Compressed H₂ and Liquid H₂ data based on use of hydroelectric power with 70% efficiency of conversion. Boustead model uses High Heating Values.

ROHM HAARS 16

2005: Analysis of multiple borate to borohydride routes in search of more efficient synthesis

Result: Energy Efficiency Summary

Pathway (metal recovery route)	Theoretical Efficiency		Primary Energy * 2015 US Grid		Primary Energy * Hydro (100%)	
	@ Heat Recovery 0%	75%	@ Heat Recovery 0%	75%	@ Heat Recovery 0%	75%
Metal Reduction						
Na (Downs w/Schlesinger)	45%	52%	9%	9%	23%	25%
Na (MCEL w/Schlesinger)	62%	76%	28%	31%	47%	54%
Mg (e-)	57%	70%	16%	17%	39%	45%
Al (carbon)	57%	67%	47%	53%	47%	53%
Ti (e-)	68%	74%	20%	21%	47%	50%
Si (carbon)	65%	70%	48%	50%	48%	50%
Zn (carbon)	76%	77%	58%	58%	58%	58%
Electrochemical Reduction						
1-step (B(OH)4- + 8e-)	71%	71%	17%	17%	50%	50%
2-step through NaBH(OCH3)3	69%	72%	24%	25%	51%	53%
Carbothermal Reduction						
Carbothermal/Elemental	75%	75%	62%	62%	62%	62%
B2O3 Reduction via Mg/Elemental	77%	82%	55%	57%	55%	57%
B2O3 Reduction via Mg/Elemental	55%	70%	38%	44%	38%	44%
Borane Routes						
BHCl2 disproportionation	37%	51%	33%	43%	33%	43%
BH(OR)2 disproportionation	56%	82%	44%	48%	44%	48%
B2O3 + M + H2	50%	53%	47%	50%	47%	50%
Metathesis						
B(OR)3 + NaAlH4	53%	65%	14%	15%	34%	38%
Formaldehyde						
Formaldehyde	54%	69%	39%	47%	39%	47%

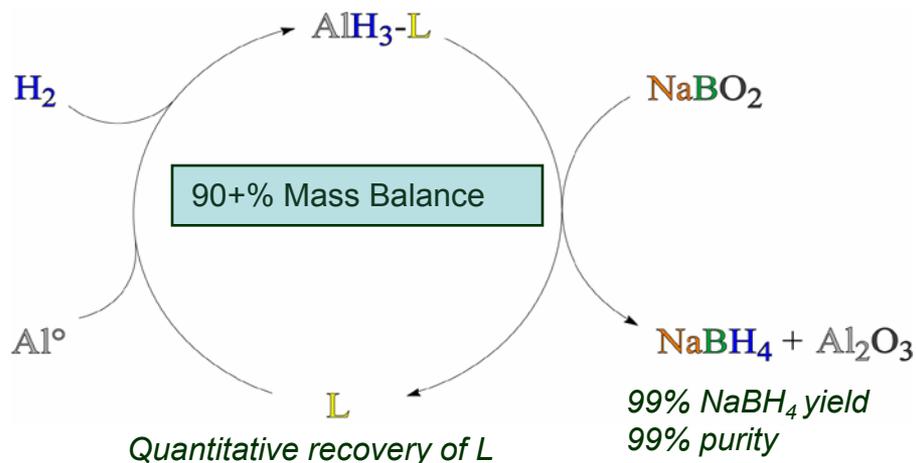
Several pathways satisfy efficiency target

Electrochemical routes require high efficiency electricity supply

Additional metrics needed to select top routes

Today: Chemically and Energy Efficient Route to NaBH₄ (implications for MHCoeE)

- NaBH₄ as precursor to many CHSCoeE and MHCoeE materials
- Carbothermal and metal reduction of borate explored as alternatives
- To be discussed ST-042, Sue Linehan (Dow)
- Solution-based metal reduction approach most promising
 - Scalable with potential use of conventional reactors and unit operations
 - All steps of reaction scheme demonstrated



Routes from NaBH₄ to NH₃BH₃ assessed

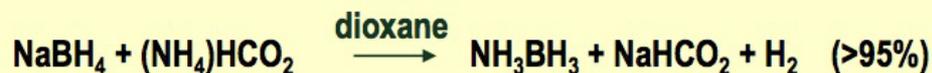
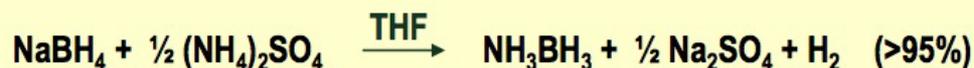
Leading First Fill AB Pathways Being Evaluated



- Metathesis of ammonium salt and MBH₄ in organic solvents

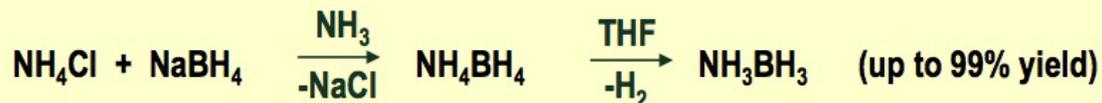


Purdue: Ramachandran et al, *Inorg. Chem*, 2007, 46, 7810-7817



Current analysis

→ PNNL: Heldebrant et al., *Energy & Envir. Science*, 2008, 1, 156-16



- Base displacement of borane complexes with ammonia



2010: Most promising pathway to AB selected

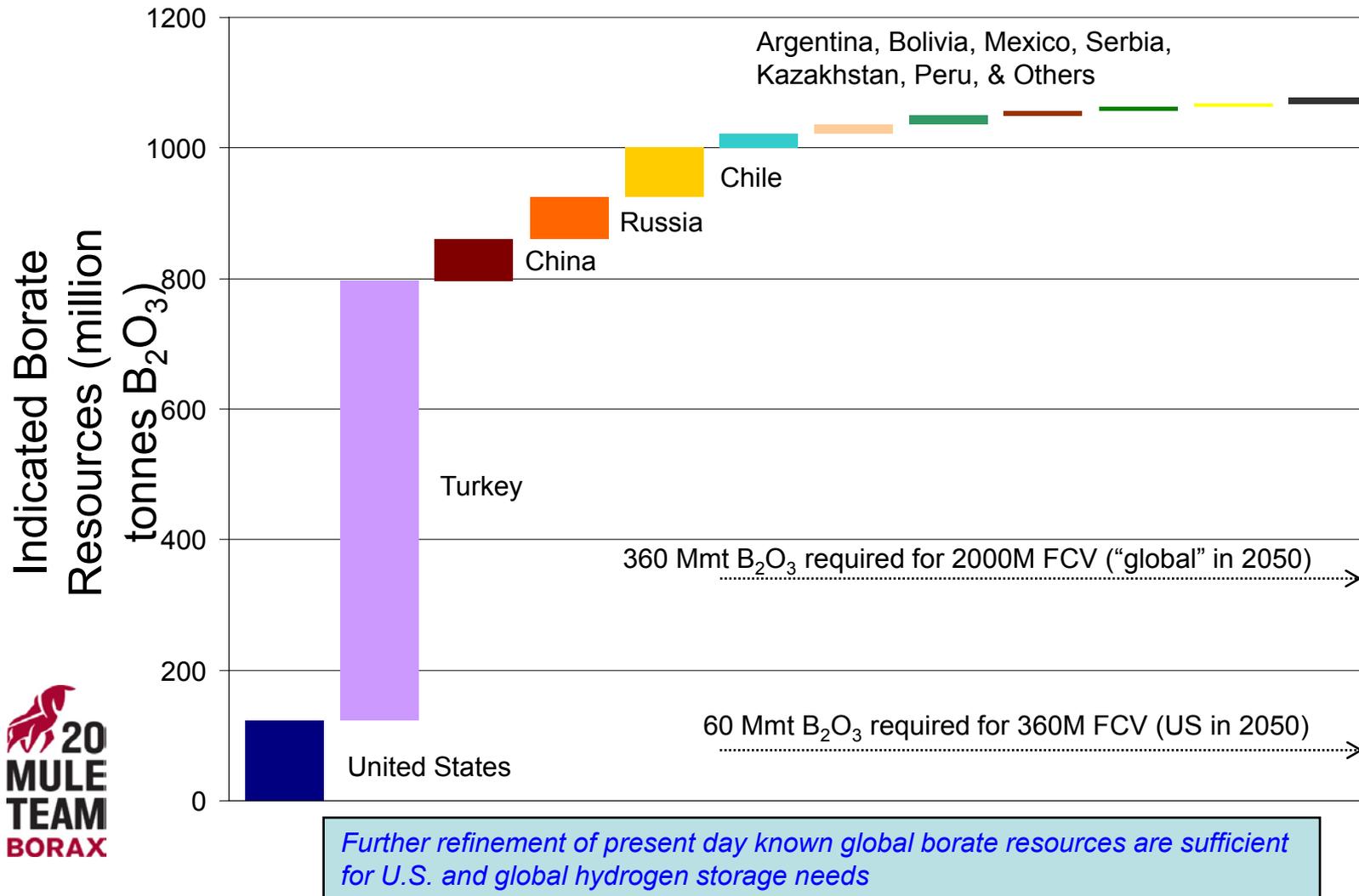
- ▶ One-pot batch reactor
 - Quantitative (isolated yields ~98%)
 - Purity (^{11}B NMR ~99%)
 - 100 gram batch reactor
 - Demonstrated 20 gram production
 - Provided partners with high purity AB
 - Parametric study indicated semi-flow reactor system possible and provided data for design

Demonstrated 20 gram batch reactor with 100 gram design capacity

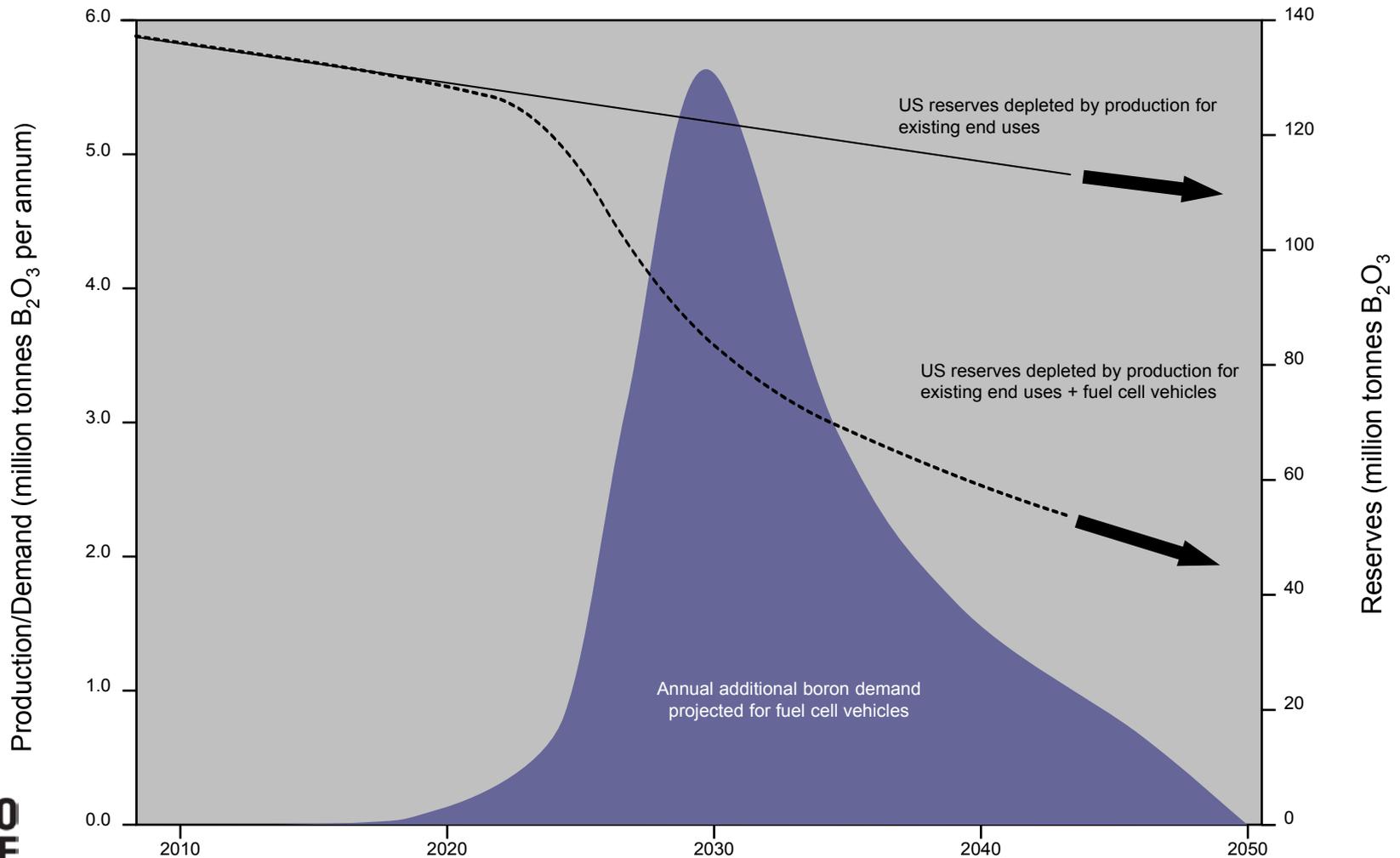
Dow's analysis indicated that high purity and yield make PNNL's synthesis superior



Borate Reserves and Chemical Hydrogen Storage (see US Borax presentation ST-043)



Resource Analysis – Boron Demand



First Fill and Regen Summary

- AB First Fill
 - **Low cost NaBH₄ is key** for producing 1st fill AB at cost required to meet 2010/2015 DOE hydrogen storage system cost targets.
 - At \$5/kg NaBH₄ price using new technology, PNNL route to AB can **produce AB on a commercial scale at about \$9/kg.**
- Low-Cost NaBH₄ for 1st Fill AB
 - Best scalable metal reduction process identified: **solution-based alane reduction route**
- AB Regeneration
 - **LANL's thiocatechol route \$7-8/kg H₂**
 - LANL's hydrazine-based pathway will **need low cost hydrazine** to be viable.
- **Boron resource adequate** to meet DOE market introduction scenarios

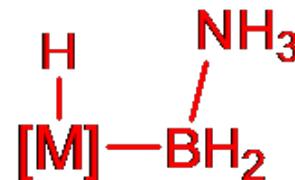
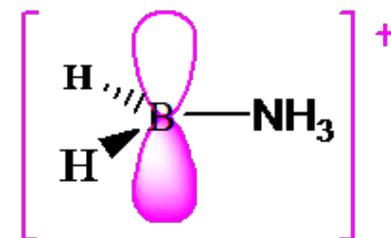
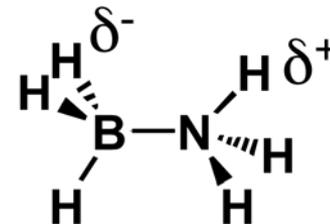
Outline for Rest of Talk

- Recap of **hydrogen release** from chemical hydrogen storage materials
 - Center's past to present accomplishments in H₂ release utilizing a variety of materials and approaches
 - Origin of the Center's down selection process for materials
 - Current status of recommendations for materials for future work

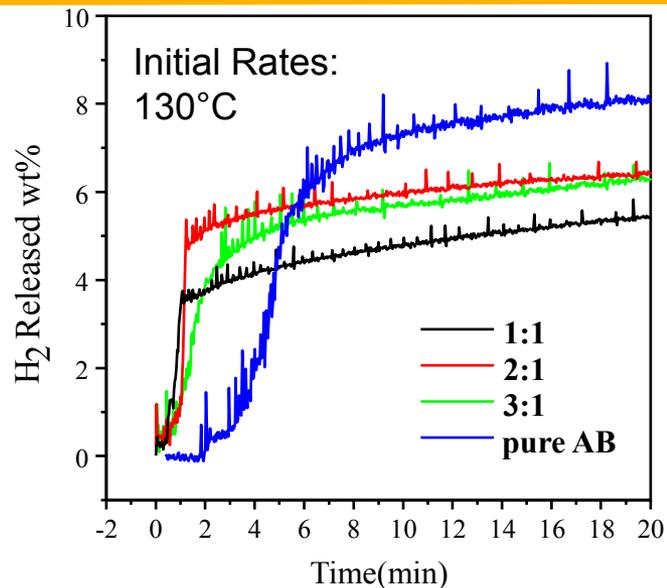
- Review of **spent fuel regeneration** progress
 - Substantial fraction of Center's resources over past three years
 - Substantial progress over last three years
 - From conceptual regen process to 7 demonstrated regeneration cycles
 - Baseline cost analysis on one process from Dow that resulted in a vastly simplified regeneration process demonstrated this year

Release: 2005 - 2006 Key Achievements for Center's Work on Ammonia Borane

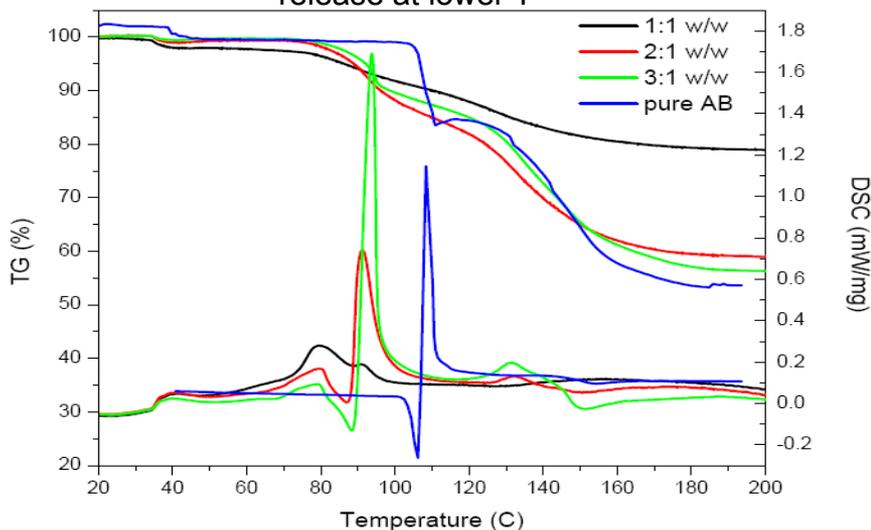
- Inclusion of AB in mesoporous materials altered rate, decreased temperature and borazine formation
- Bronstead acid catalysts released >1 eq. H_2
- Rapid room temperature release of 1 eq. H_2 using Ir catalysts
- Up to 2 eq. H_2 released at moderate temperatures using homogeneous electron-rich precious metal complexes
- The first examples of *non-precious metal catalysts* for AB release discovered
- Ionic liquid/ammonia borane mixtures open up new reaction pathways with high rates
- Kinetics and mechanistic studies were underway



Use of Mesoporous 'Scaffolds' to Increase Rate of Release and Suppress Foaming



DSC/TGA ramp at 1K/min: Scaffolds release at lower T



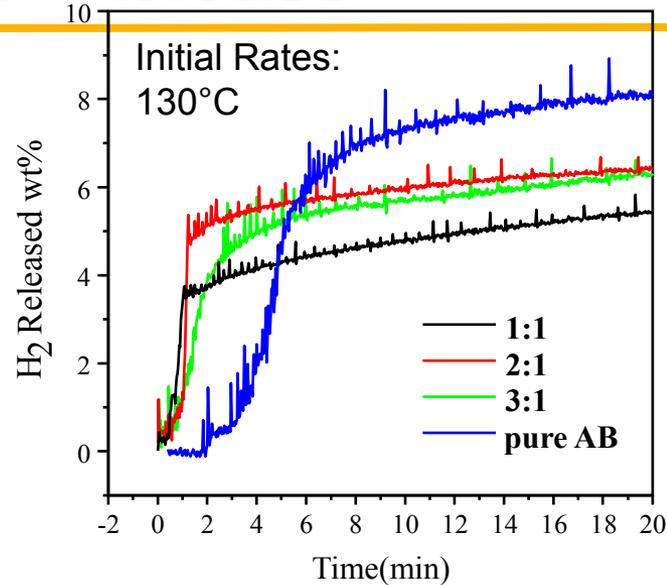
Study completed looking at effect of various scaffold materials on hydrogen release from AB

- silica outperformed carbon, aluminosilicate, and titania scaffolds
- **diminished induction period and increased release kinetics** when AB added at less than 4:1 ratio with scaffold
- **scaffolds suppress foaming of AB**

3:1 AB:silica looks most promising to maintain high capacity while benefiting from thermodynamics and kinetics of scaffold materials

- **increases rate by a factor of 6**
- **decreases release temperature to 95°C**

Use of Mesoporous 'Scaffolds' to Increase Rate of Release



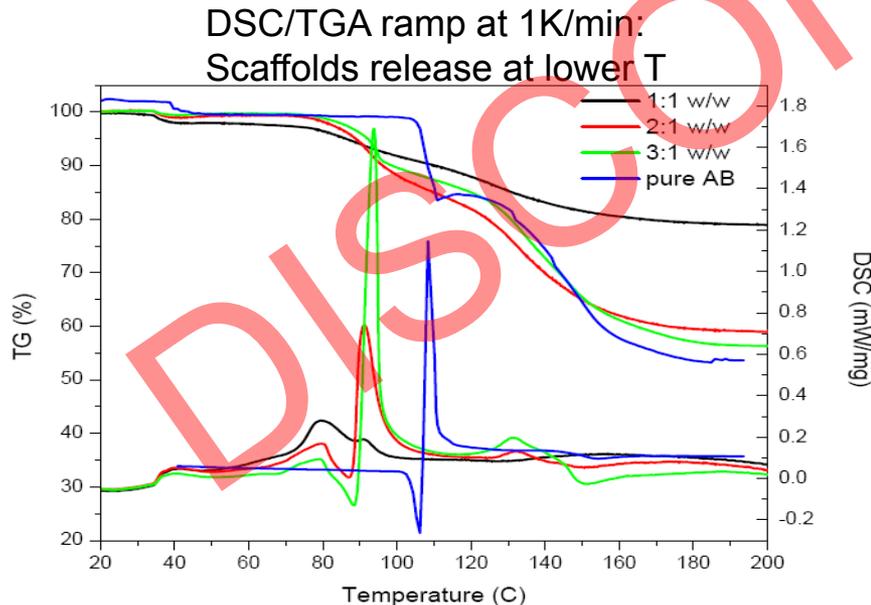
Study completed looking at effect of various scaffold materials on hydrogen release from AB

- silica outperformed carbon, aluminosilicate, and titania scaffolds

- diminished induction period and increased kinetics when AB added at less than 4:1 ratio with scaffold

- scaffolds suppress foaming of AB

3:1 AB:silica looks most promising to maintain high capacity while benefiting from thermodynamics and kinetics of scaffold materials



Gravimetric Penalty of Scaffold

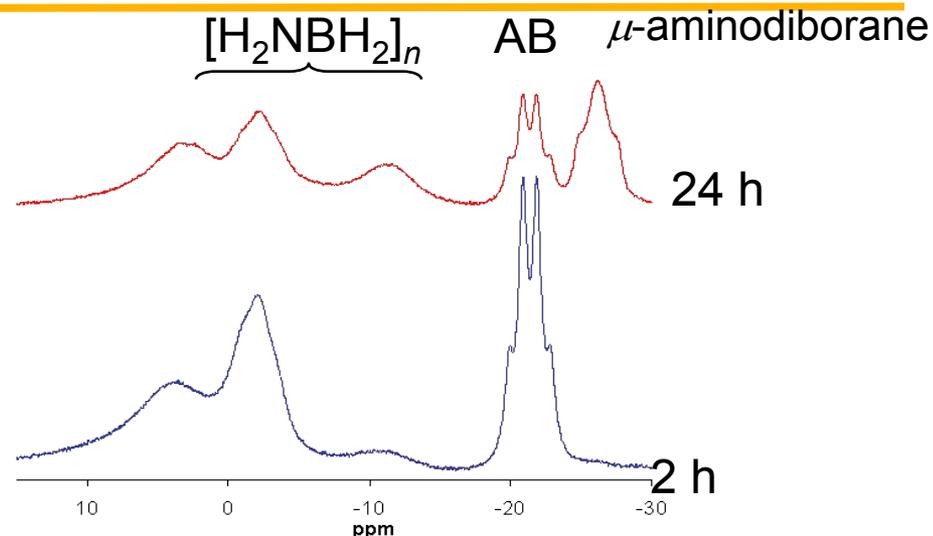
decreases release temperature to 95°C

Pacific Northwest
National Laboratory

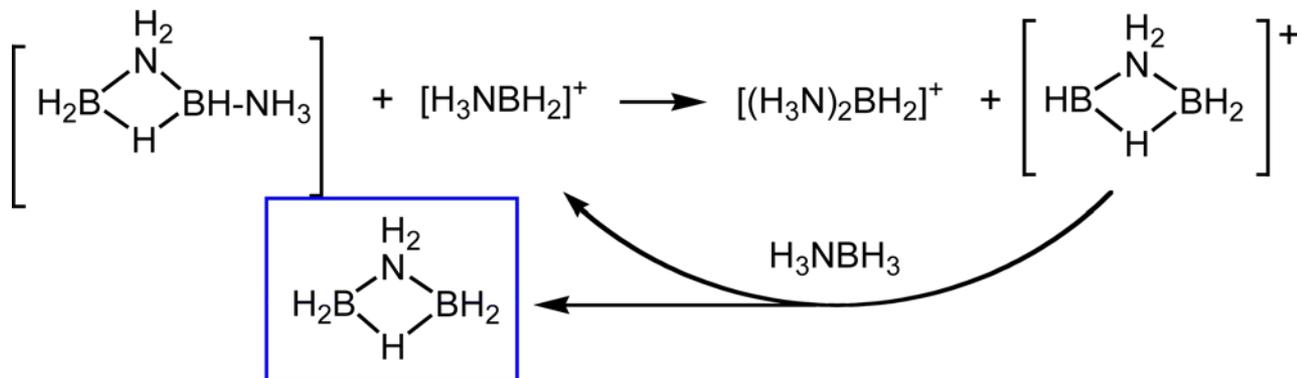
Operated by Battelle for the
U.S. Department of Energy

2006 Results: Bronstead Acid Catalysis

- Strong Bronsted and Lewis acids enable H₂ **release at room temp**
- Experimental and theory studies (w/ Alabama):
 - cationic initiator
 - acyclic BNH_x products
 - < 1 eq. hydrogen, due to μ-aminodiborane by-product
 - **By-product formation leads to free NH₃ which quenches cation and chain propagation**



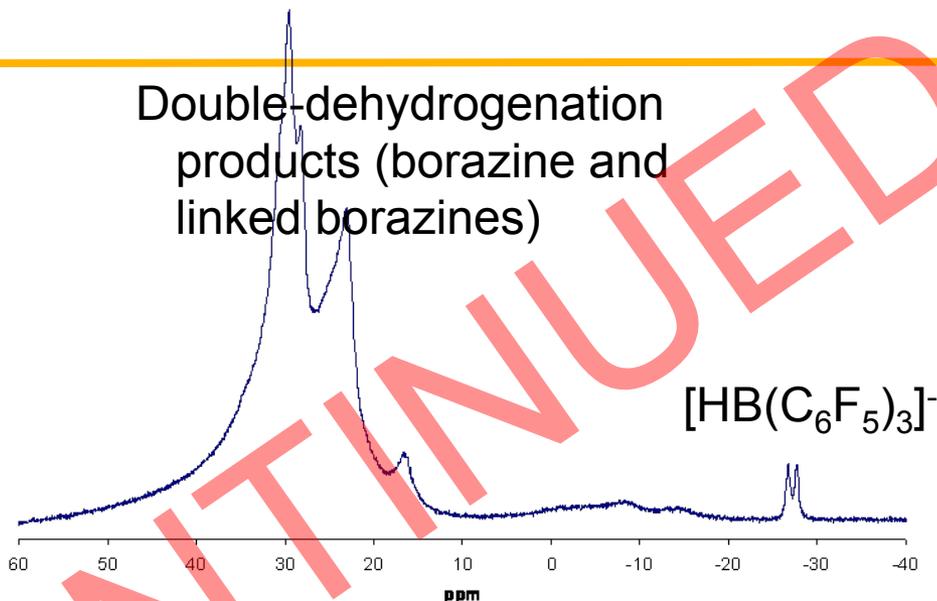
H-coupled ¹¹B NMR of AB and 0.1 equiv. triflic acid in diglyme at 24°C



Acid Catalysis: Concentration Effects

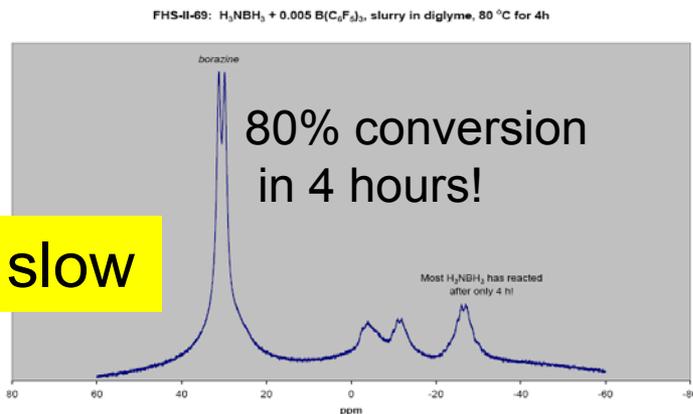
- Reducing acid/AB ratio eliminates μ -aminodiborane and affords $> 2 \text{ H}_2$
- Reducing amount of solvent gives faster rates but volatile borazine is major product

Double-dehydrogenation products (borazine and linked borazines)



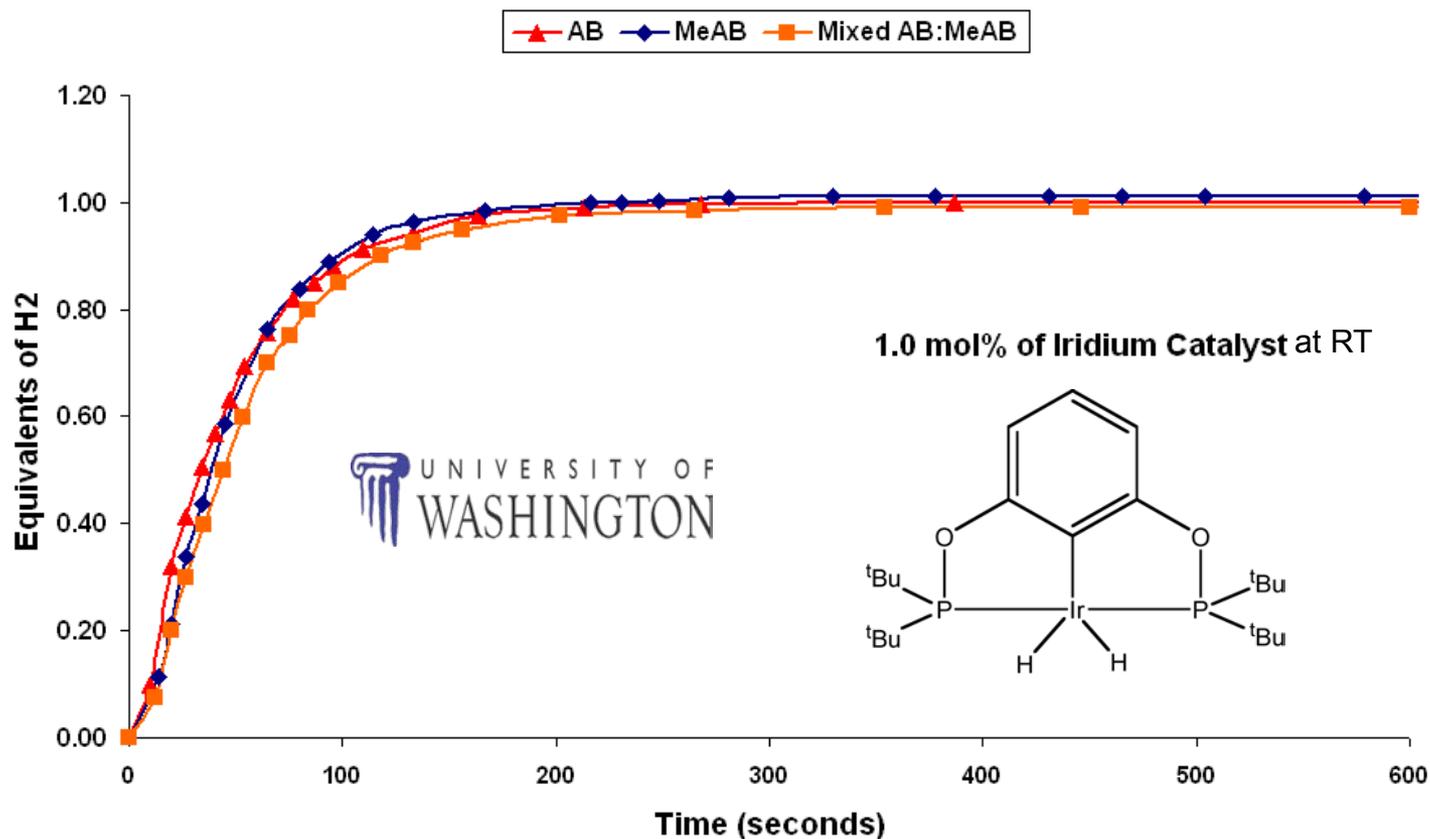
H-coupled ^{11}B NMR of AB and 0.005 eq. $\text{B}(\text{C}_6\text{F}_5)_3$ in diglyme at 80°C

Rates too slow



Washington Demonstrates Rapid Release at RT!

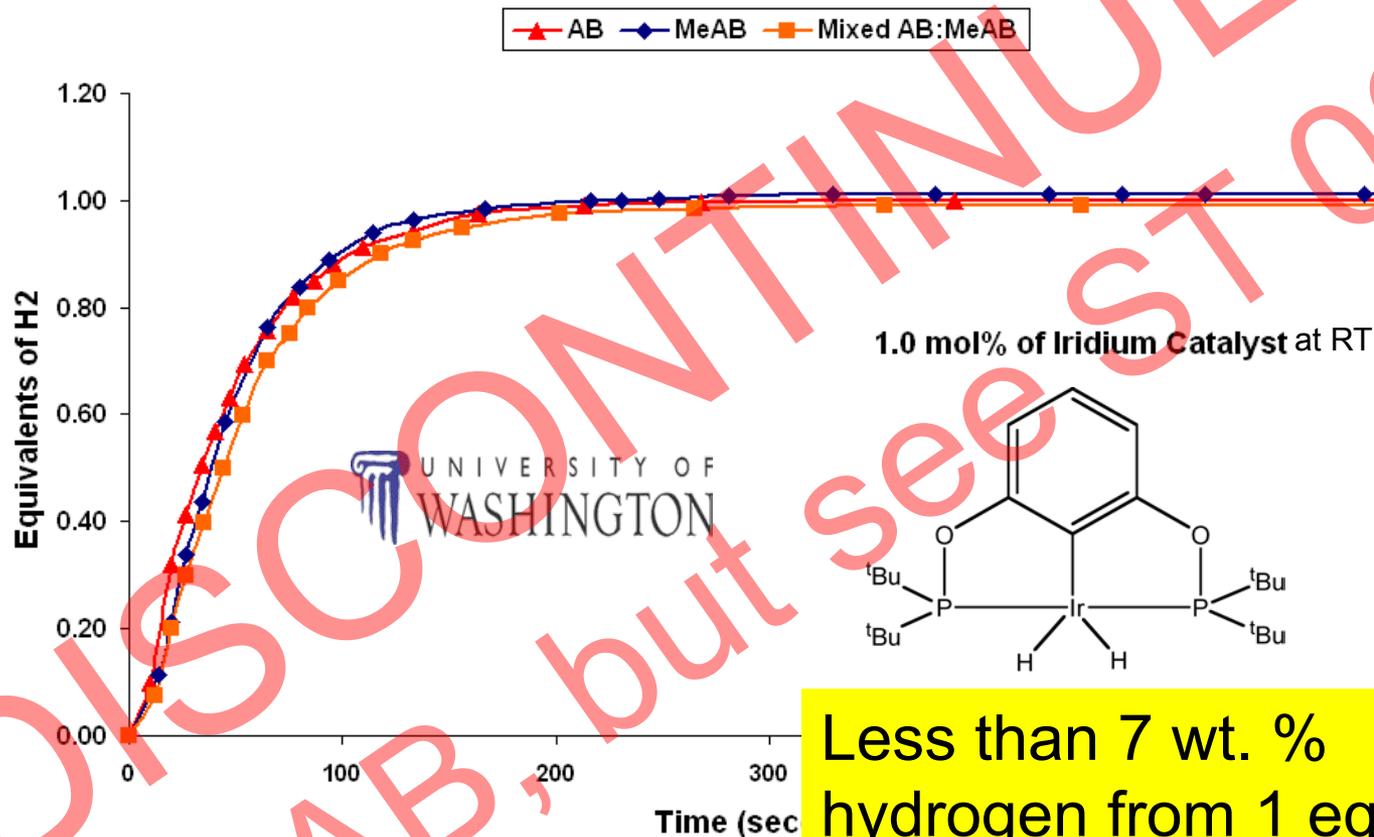
Dehydrogenation of BN Compounds by Iridium



- ✓ Ir catalyst promotes release of H₂ from different BN systems at similar rates allowing for potential development of mixed BN materials for hydrogen storage applications

Washington Demonstrates Rapid Release at RT!

Dehydrogenation of BN Compounds by Iridium



✓ Ir catalyst promotes release of H₂ from different BN systems at similar rates allowing for potential development of mixed BN materials for hydrogen storage applications

Homogeneous Catalysts: Transition Metal Carbene Ligand Complexes

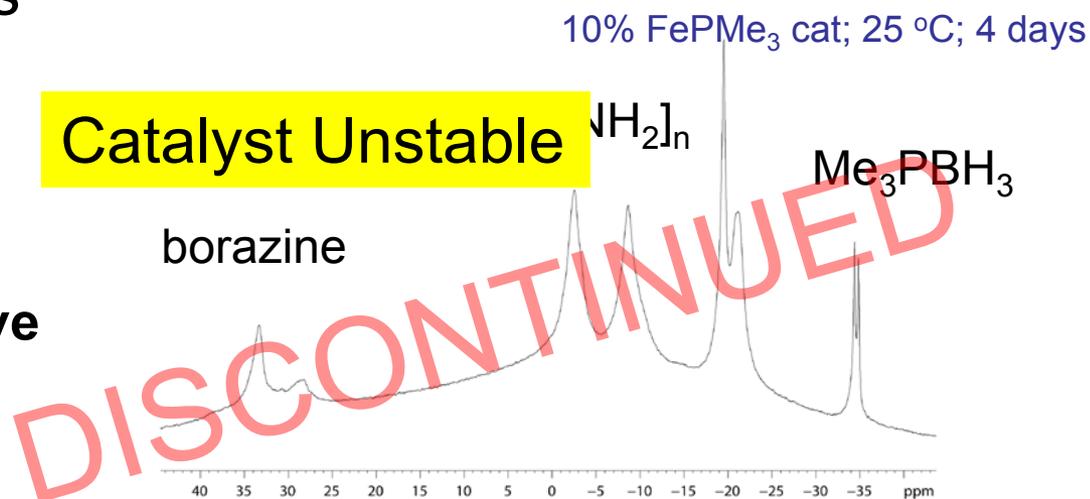
APPROACH

- Examine electron-rich metal complexes
- Base metal complexes with electron-rich phosphine and carbene ligands

RESULTS

- Iron and nickel phosphine complexes are slow and **short-lived due to inactive metal boride formation**
- **Metal carbene complexes afford long-lived catalysts** that afford linked borazines without build-up of $[\text{BH}_2\text{NH}_2]_n$ intermediates

Catalyst Unstable



Heterogeneous catalysts found to be faster, more readily engineered into system

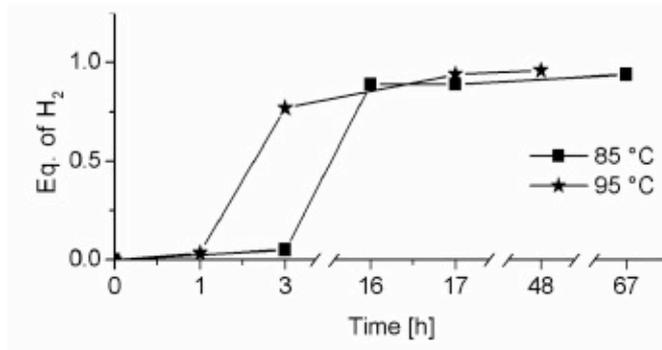
2006: Penn show that Ionic Liquid (IL) media assists H₂ release from AB



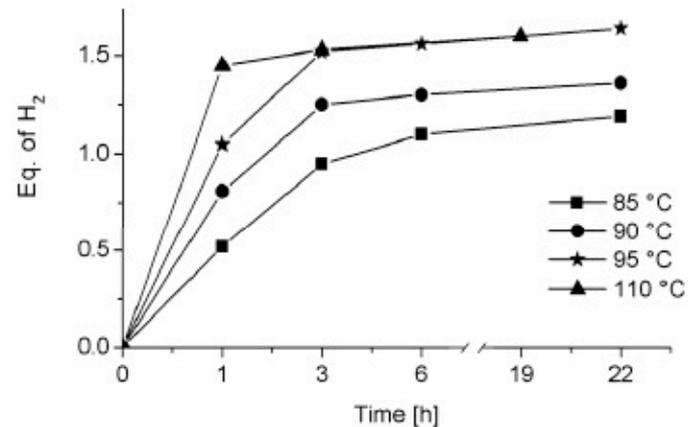
Summary of Ionic Liquid Studies



Neat NH₃BH₃



NH₃BH₃ + Ionic Liquid[‡]



[‡] 1-Butyl-3-methylimidazolium chloride

Ionic liquids accelerate the hydrogen release from NH₃BH₃!

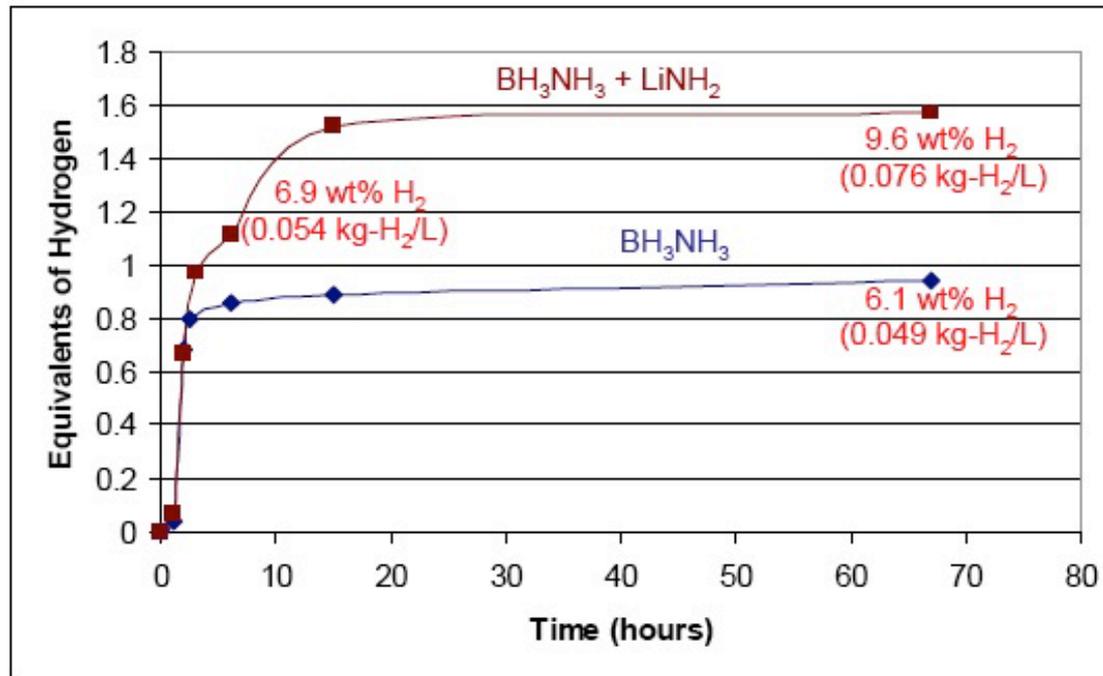
2006: First Hints that M-ABs Could be Interesting



Enhanced Hydrogen Release with LiNH_2



$\text{BH}_3\text{NH}_3 + 10 \text{ mol } \% \text{LiNH}_2$ at $85 \text{ }^\circ\text{C}$



2007/2008: Key Decision Points for Center

- SBH: DOE Go/No-Go September 2007
 - Result would also have bearing on the hydrolysis of polyhedral boron hydrides
- Center-Wide Downselect of Materials November 2007
 - Fully formulated down select decision tree
 - Key results of down select process
- Partners were down selected by consideration of remaining materials vs. partner capabilities

Milestones and Go/ No Go Decisions

2007 DOE Sodium Borohydride (SBH) Hydrolysis Go/ No-Go Decision for Onboard Release

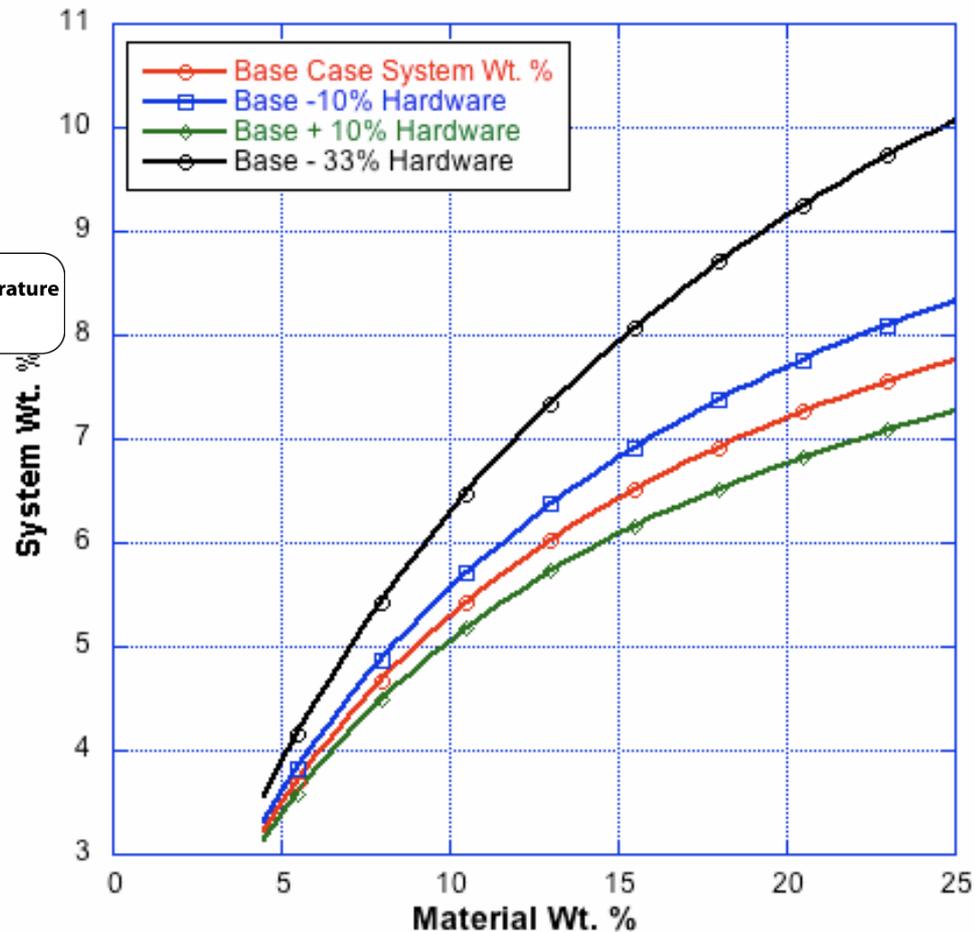
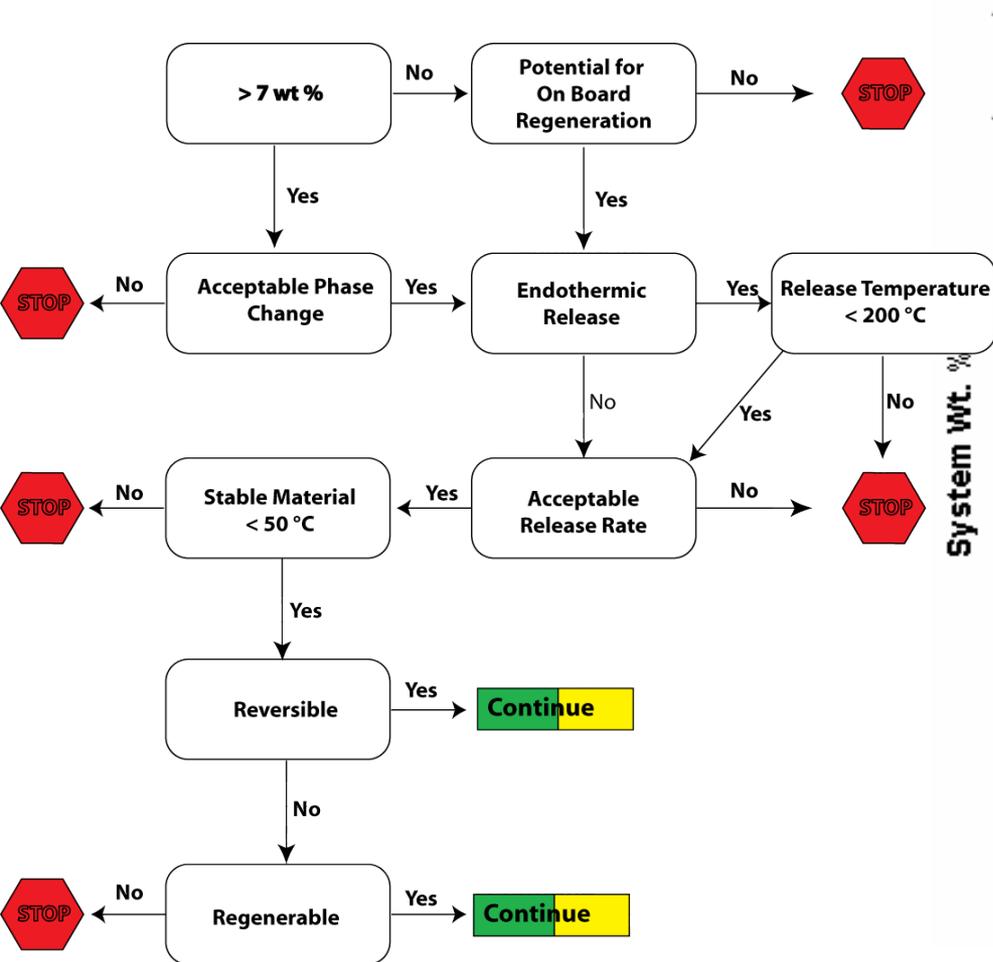
- Recommendations
 - **No-Go for hydrolysis of SBH** for on-board vehicular H₂ storage
 - Insufficient capacity
 - **Solubility of spent fuel – borate crystallized from solution; energy efficient regeneration of borates** were secondary issues
 - Continue research activities on low cost NaBH₄ pathways (Rohm&Haas)
- **Go/No Go process provided valuable experience** in understanding the life cycle of a chemical hydrogen storage system
 - Data requirements
 - Analysis assumptions
 - Contributed to developing Center down select processes

Identify showstoppers early – FAIL FAST

Avoid liquid to solid phase changes in spent fuel

Avoid regenerating stable spent fuel bonds back to B-H bonds

System Gravimetric Guiding Rule Developed from SBH G/NG Experience -- 2007



$$\text{System Wt}\% = \frac{\text{Hydrogen Mass}}{\text{Hardware Mass} + \frac{\text{Hydrogen Mass}}{\text{Material Wt}\%}}$$

2007/8 Output from Decision Tree Mediated Down Select Process

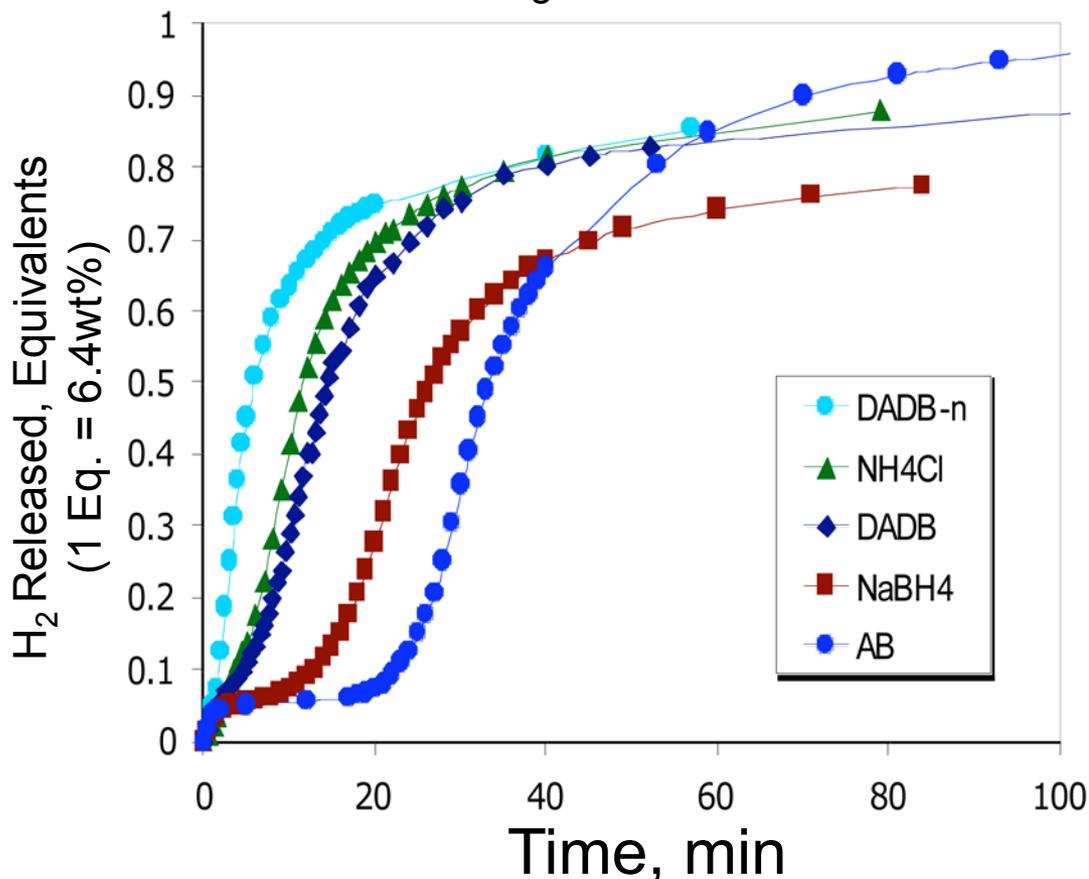
- By 2007, CHSCoE investigated more than 60 materials or classes of materials
- 50% Deselected
 - Endothermic organic compounds (low capacity)
 - Nanoparticles (low capacity)
 - Magnesium alkoxide/hydrolysis (release temp > 200 °C)
 - SBH (liquid to solid phase change during release)
 - Bronsted acid catalyzed release from ammonia borane (slow)
 - Substoichiometric LiH/AB mixtures (better compositions found)
 - Ammonia borane/solvent mixtures < 50 wt. % AB (capacity)
 - Polyhedral boranes (requires regen of borate B-O bonds to B-H)
- 30% Conditionally down selected, need resolution of certain performance concerns -- e.g. carbenes, methylamine borane, certain metal amidoboranes
- 20% Down selected for priority development -- e.g. ammonia borane, some metal amidoboranes, certain alkylamine boranes
- Redirected partners involved in SBH/hydrolysis to first fill, regeneration efforts, and new materials exploration

2007/2008 Key Results: AB Hydrogen Release

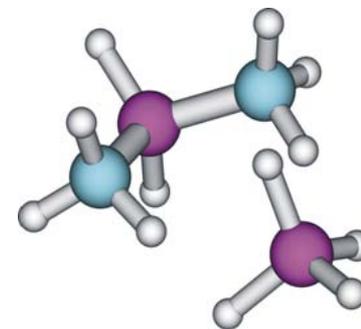
- Thermolysis/Chemical Promoters
 - Anionic polymerization **mechanism enhances extent, rates of release**
 - Ionic liquids **avoid induction period**, promote reactivity, improve rates and extent of release from AB
 - Chemical **promoters alter reaction pathway**, enhance extent of release
- Solid AB Thermolysis
 - Mechanistic understanding of release from solid AB
 - Chemical additives reduce induction period, **alter 'nucleation and growth' phase**
 - **Demonstrated up to 16 wt. % H₂**
 - Fuel stability studies ongoing
- Metal Catalysis
 - Improved **mechanistic understanding drives catalyst design**
 - Equally rapid release of 1 H₂ from AB and MeAB with Ir catalysts at room temperature
 - Greater extent of H₂ with inexpensive **base metal catalysts at improved rates** at T > 60 °C (patents)
 - **Liquid fuel** compositions: MeAB/AB
 - MeAB/AB release rates and capacities improving with better catalysts
 - MeAB dehydrogenation (-1H₂) results in **soluble spent fuel** products
- 2007 Go/No Go Decision Point for SBH Hydrolysis

2007: Additives Increase Release Rate

100°C – gas burette studies



DADB



Additives reduce the induction period

Neat DADB → fastest kinetics

BH₄⁻ & NH₄⁺ improve kinetics

NH₄Cl is slightly better than DADB at 5% loading

Acidic character appears to be important for the additive → consistent with mechanistic work

Key result: additives to AB formulation accelerate release

2007: Stability & Exothermic Release

DOE target for 2015: fuel needs to be stable at 60°C

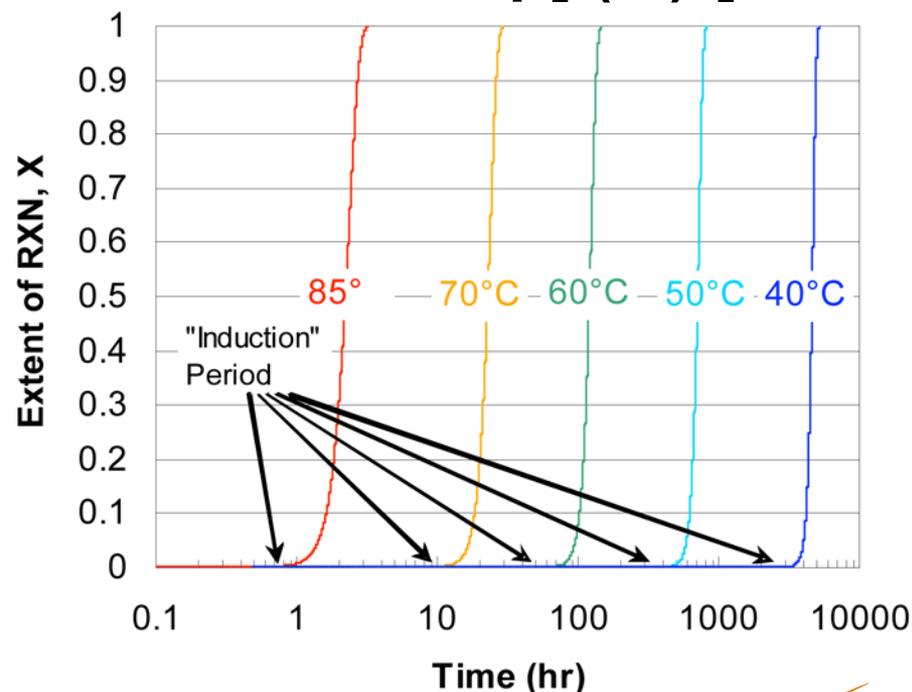
Solid ammonia borane shows an induction period before release

Adiabatic assumed as a worst case

- Fuel predicted to be stable for ~ 100 hrs. at 60°C
- Greater stability at lower T

Avrami Kinetics

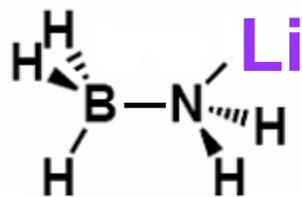
$$X = 1 - \exp[-(kt)^n]$$



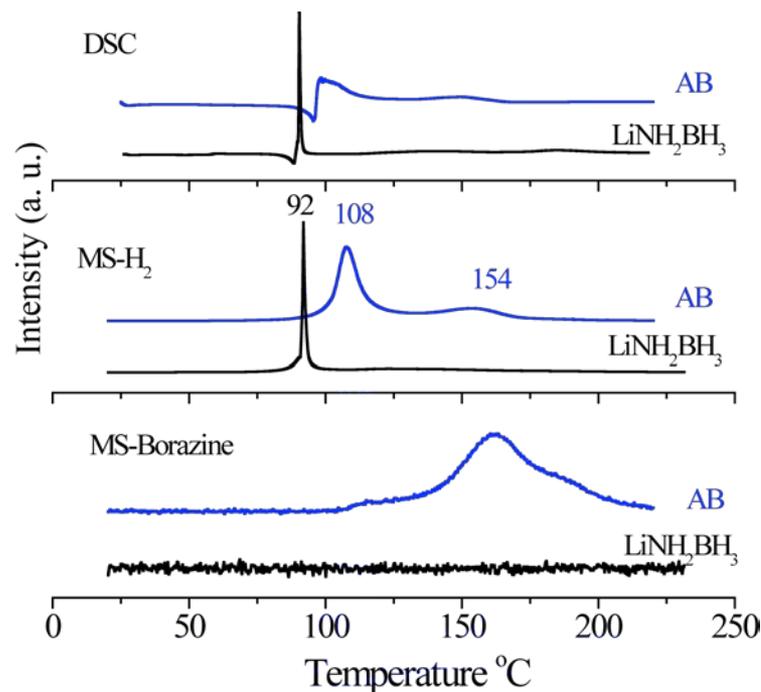
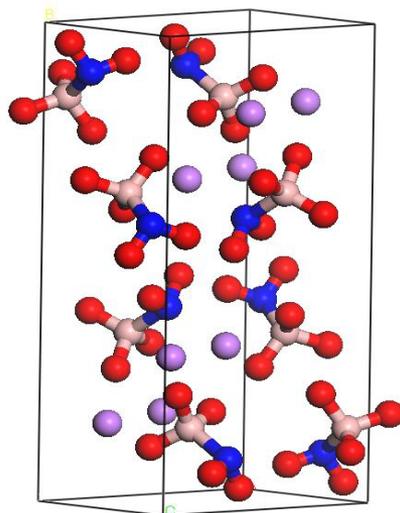
2006: conservative model predicted stability issues for storage at 50-60°C

2007: Metal Amidoboranes – Focus of an IPHE Storage Project

- Release of 2 equivalents (~11 wt%) of hydrogen below 100°C
- No borazine impurity in the hydrogen released
- Faster kinetics for a given wt% than ammonia borane



Red – H
Blue – N
Pink – B
Purple – Li



PNNL – solid state routes to new materials

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

M-ABs: A Search for Less Exothermic Release Systems; LANL Extends Series via Solution-Based Syntheses

AB derivative	H ₂ wt%
LiNH ₂ BH ₃	13.70 (2008)
Ti(NH ₂ BH ₃) ₄	12.05
Mg(NH ₂ BH ₃) ₂	12.00
Sc(NH ₂ BH ₃) ₃	11.24
Li ₂ [Zn(NH ₂ BH ₃) ₄]	10.15
Ca(NH ₂ BH ₃) ₂	10.10 (2008)
NaNH ₂ BH ₃	9.54 (2008)
LiZn(NH ₂ BH ₃) ₃	9.34
Zn(NH ₂ BH ₃) ₂	8.06
KNH ₂ BH ₃	7.31 (2009)
Al(NH ₂ BH ₃) ₃	12.97 (2009)



M-ABs: A Search for Less Exothermic Release Systems; LANL Extends Series via Solution-Based Syntheses

All monometallic MABs studied to date are too exothermic for onboard regeneration; no path forward for chemical regeneration at this time

$\text{Ti}(\text{NH}_2\text{BH}_3)_4$	12.05
$\text{Mg}(\text{NH}_2\text{BH}_3)_2$	12.00
$\text{Sc}(\text{NH}_2\text{BH}_3)_3$	11.24
$\text{Li}_2[\text{Zn}(\text{NH}_2\text{BH}_3)]_4$	10.15
$\text{Ca}(\text{NH}_2\text{BH}_3)_2$	10.10 (2008)
NaNH_2BH_3	9.54 (2008)
$\text{LiZn}(\text{NH}_2\text{BH}_3)_3$	9.34
$\text{Zn}(\text{NH}_2\text{BH}_3)_2$	8.06
KNH_2BH_3	7.31 (2009)
$\text{Al}(\text{NH}_2\text{BH}_3)_3$	12.97 (2009)

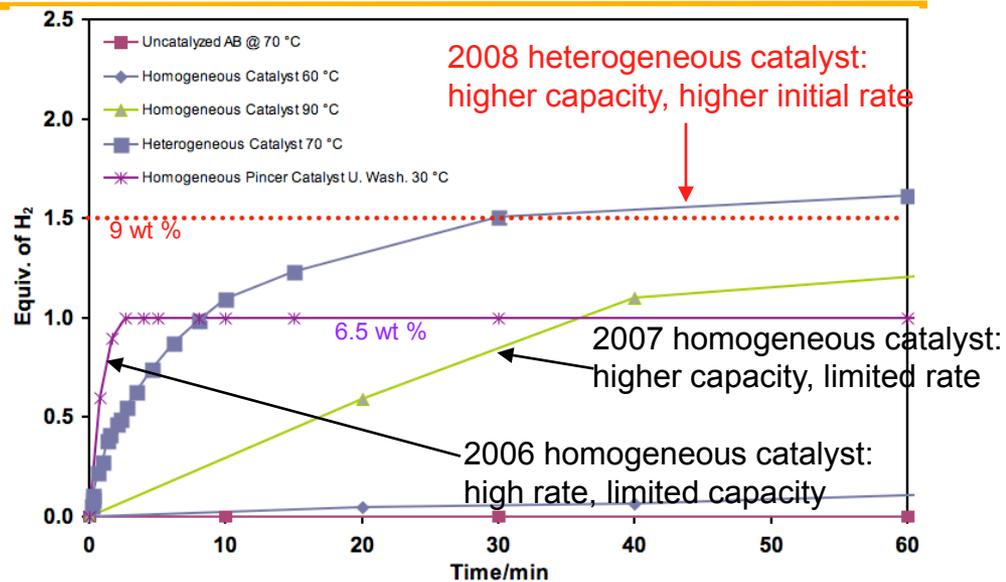


Search for binary M, M' ABs of reduced exothermicity continues

2008/2009 Progress: Catalytic Release of Hydrogen from Ammonia Borane

Accomplishments

- Developed **catalytic release of hydrogen at higher than target rates** and quantities approaching 2 equivalents of hydrogen/AB (>10 wt. %)
- Gained an understanding of spent fuels properties vs. release mechanism that impacts regeneration chemistries
- Discovered **liquid mixtures of AB** derivatives that release hydrogen similarly to AB
- Demonstrated **heterogeneous catalytic release with initial rates higher than the target rates (4 times our 2006 rates)** and quantities of H₂ released approaching 2 equivalents/AB (*ca. 2 times our 2006 capacities*)



Impact

- Catalysts increase rate and capacity, toward reducing system cost
- Liquid fuels enable greater range of hydrogen release engineering opportunities
- **Heterogeneous catalysts are readily separable from liquid spent fuel**, and preclude catalyst separations costs in the regeneration steps

2009 Accomplishments: Anti-foaming agents for solid ammonia borane with acceptable mass penalty

- Solid AB foams significantly with release of 1st eq H₂
- Explored over 30 different additives; methyl cellulose selected



15wt% MC/AB

15wt% MC/AB heated to 180 °C

10wt% MC/AB heated to 180 °C

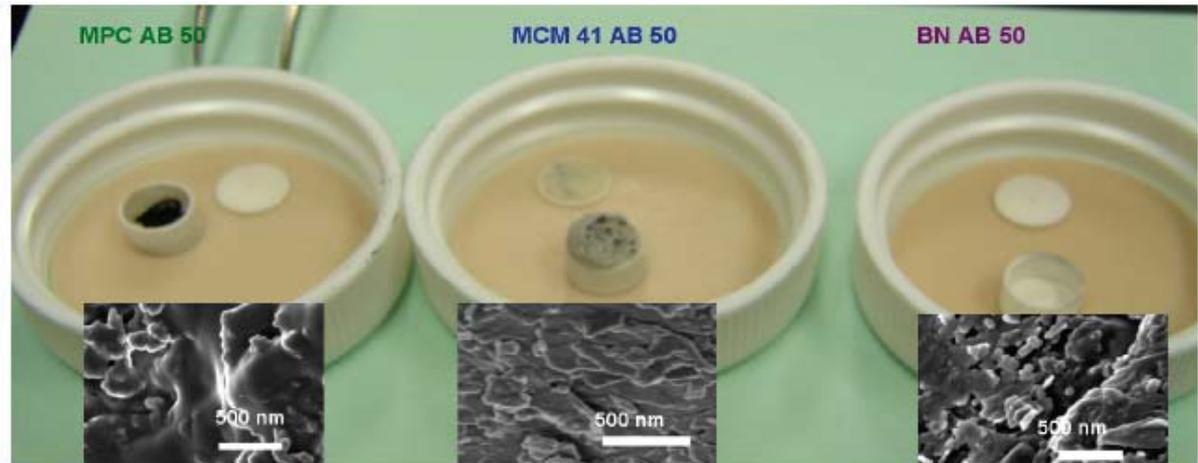
15wt% MC/AB (T2) heated to 180°C

Neat AB heated to 180°C

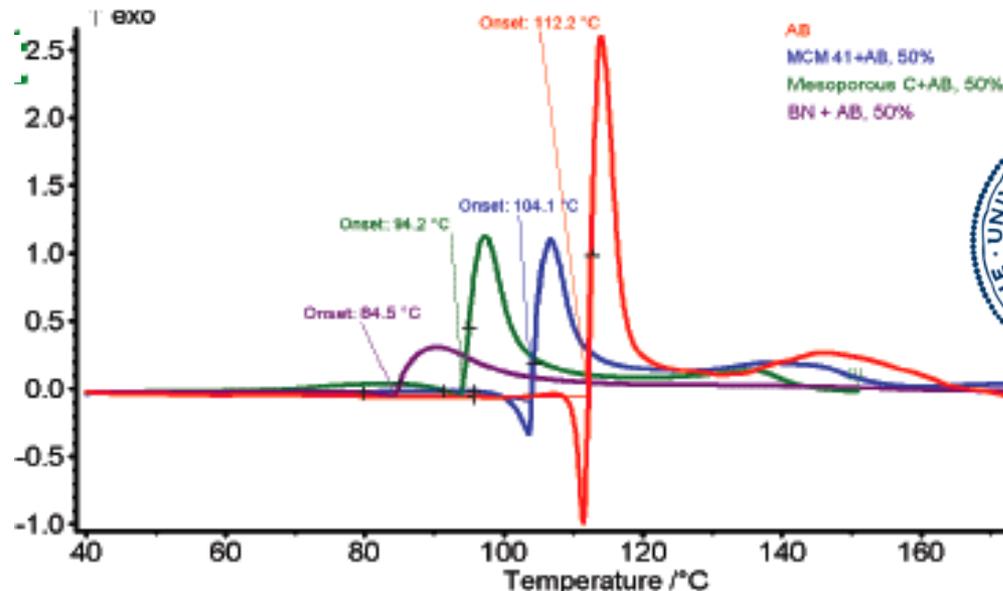
Best case: 10-20 wt% of methyl cellulose (MC) prevents foaming with proper preparation.

2009 Nanomaterial Supports for Hydrogen Release from Ammonia Borane (AB)

Some nanomaterials **reduce foaming**: MPC (mesoporous carbon), MCM 41, and nano-BN are shown and only MPC and nano-BN show an absence of foaming after hydrogen release.



Nanomaterial supports **reduce temperature for dehydrogenation** as well as exothermicity of release: DSC trace of the various combinations normalized for AB. Nano-BN shows the best results.

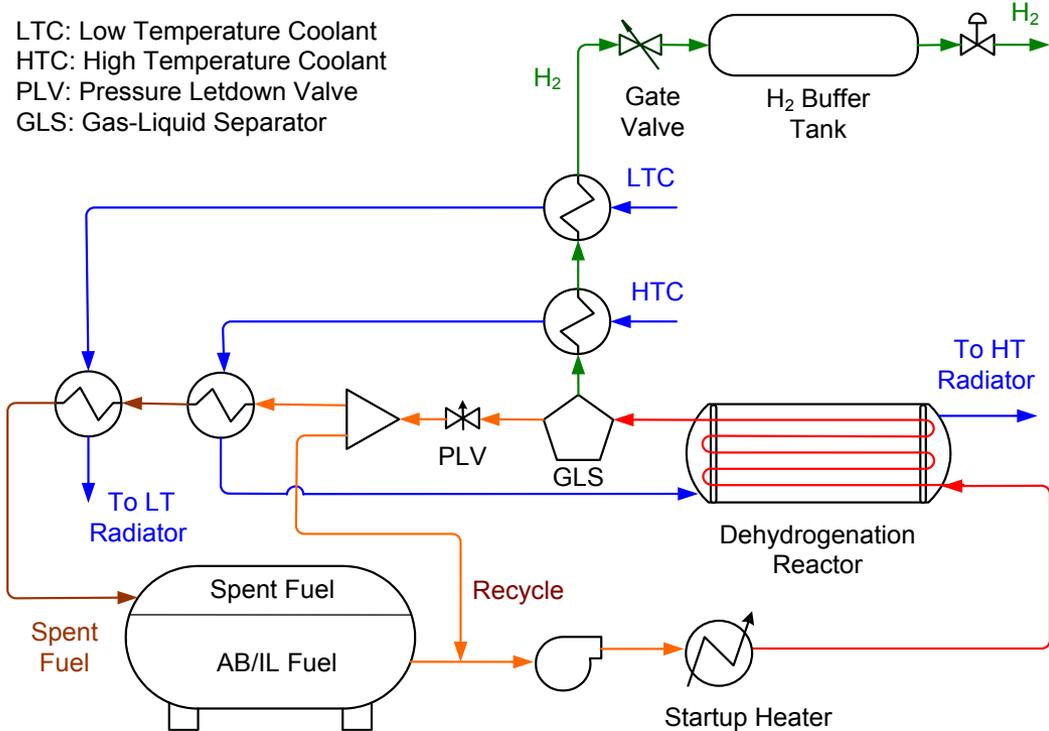
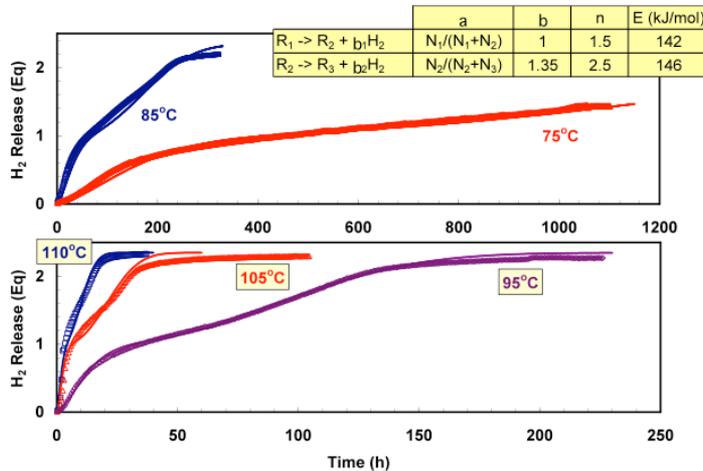


2009 Hydrogen Release

- Chemical hydrogen storage materials that we have downselected for further study have demonstrated
 - Capacities that exceed 10 wt. %
 - Temperatures of release that range from 70 – 160 °C and have
 - Kinetics of release that can exceed DOE technical targets
- Progress in release 2010
 - **Impurities – moved from qualitative to quantitative analysis**
 - **More focus on reaction engineering to minimize impurity formation**
 - **Developing mixtures of fuels that may remain liquid over broad temperatures**
- Liquid fuels – alkylamineborane/AB mixtures **poison** current heterogeneous **catalysts.** **DISCONTINUED**
- **Focus on AB/Ionic Liquid systems continues**

Preliminary Analysis of Onboard Ionic Liquid/AB Release System by ANL

Onboard release system: ANL analysing an onboard liquid fuel developed in Sneddon's group at U. Penn based on ionic liquid/ammonia borane mixtures with capacities up to 11 wt. %, and fast release rates above 85 °C

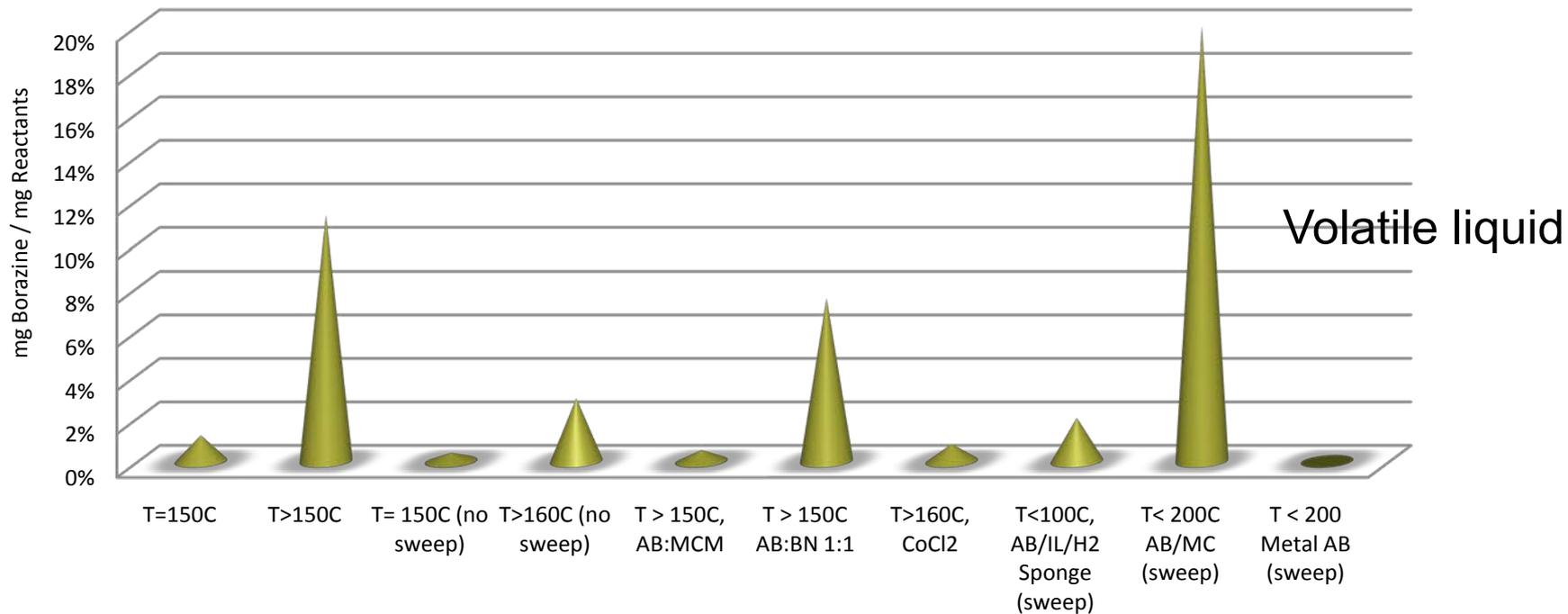


- ✓ Substantial spent fuel recycle to manage exothermic release
- ✓ Heat rejection and startup/shutdown are key challenges

Gas Phase Impurities Released from AB

- PNNL and LANL are working together to determine measurement and analytical techniques to accurately quantify impurities including the time evolution or impurity release (NH_3 , borazine, diborane).

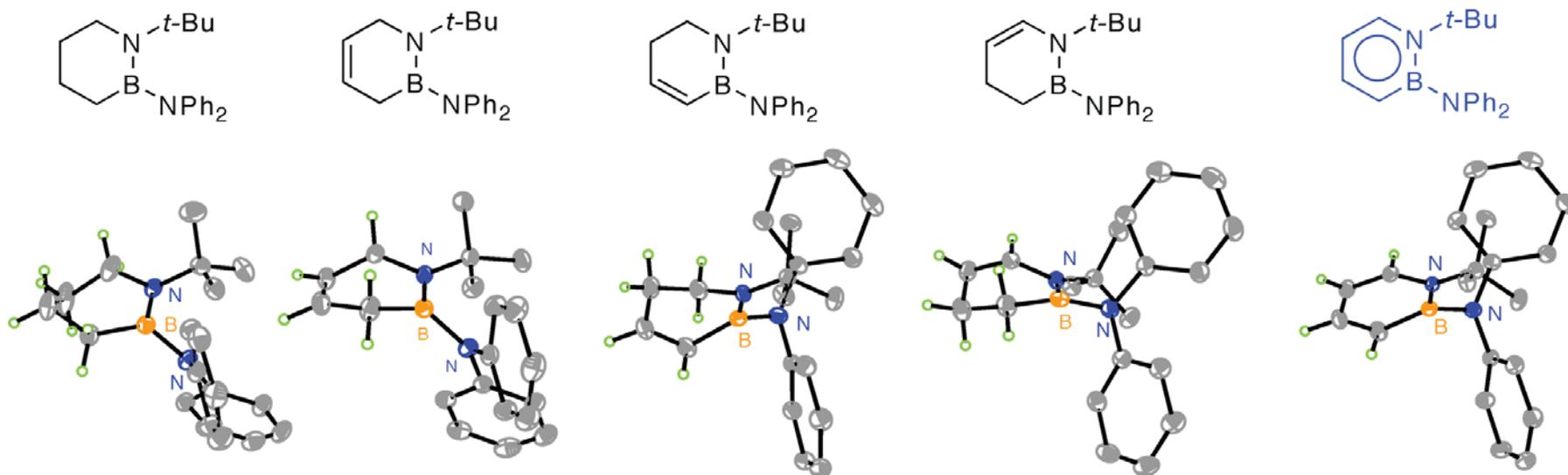
Borazine Release at 1 Bar



Additives and catalysts mitigate borazine release into gas phase

2008/2009: New Materials from U. Oregon

- New project within the Center – U. Oregon's cyclo- CBN compounds
 - synthesized additional CBN heterocycle materials



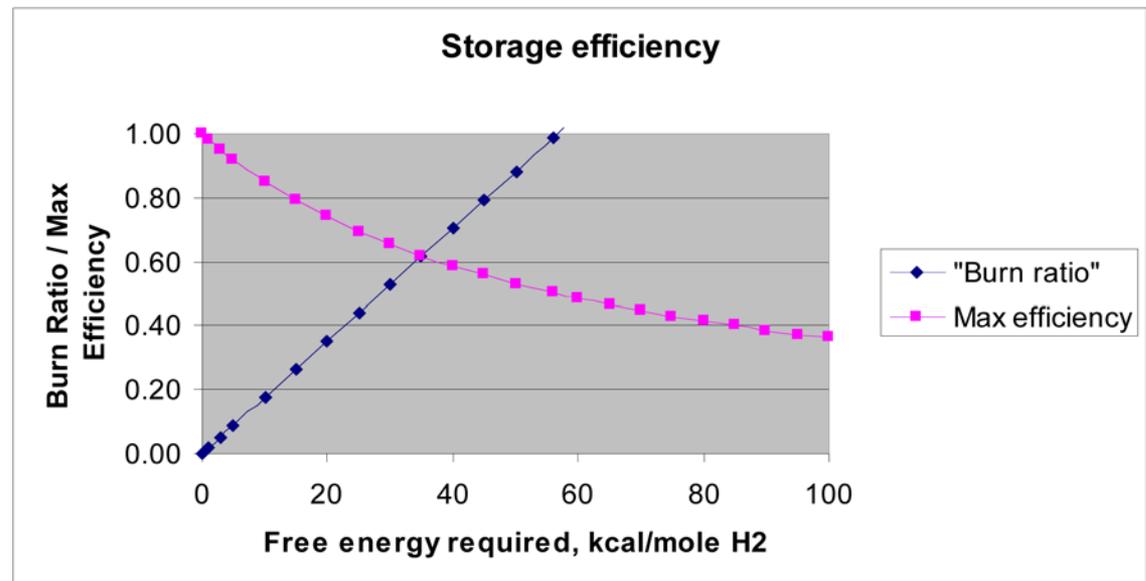
Coupling of endothermic CH with exothermic BNH release

- New AB/MH_n AB/M'BH₄ compositions from PNNL
 - Exothermic AB + endothermic MH or MBH₄ mixtures

Regeneration – the Achilles Heel of Chemical Hydrogen Storage

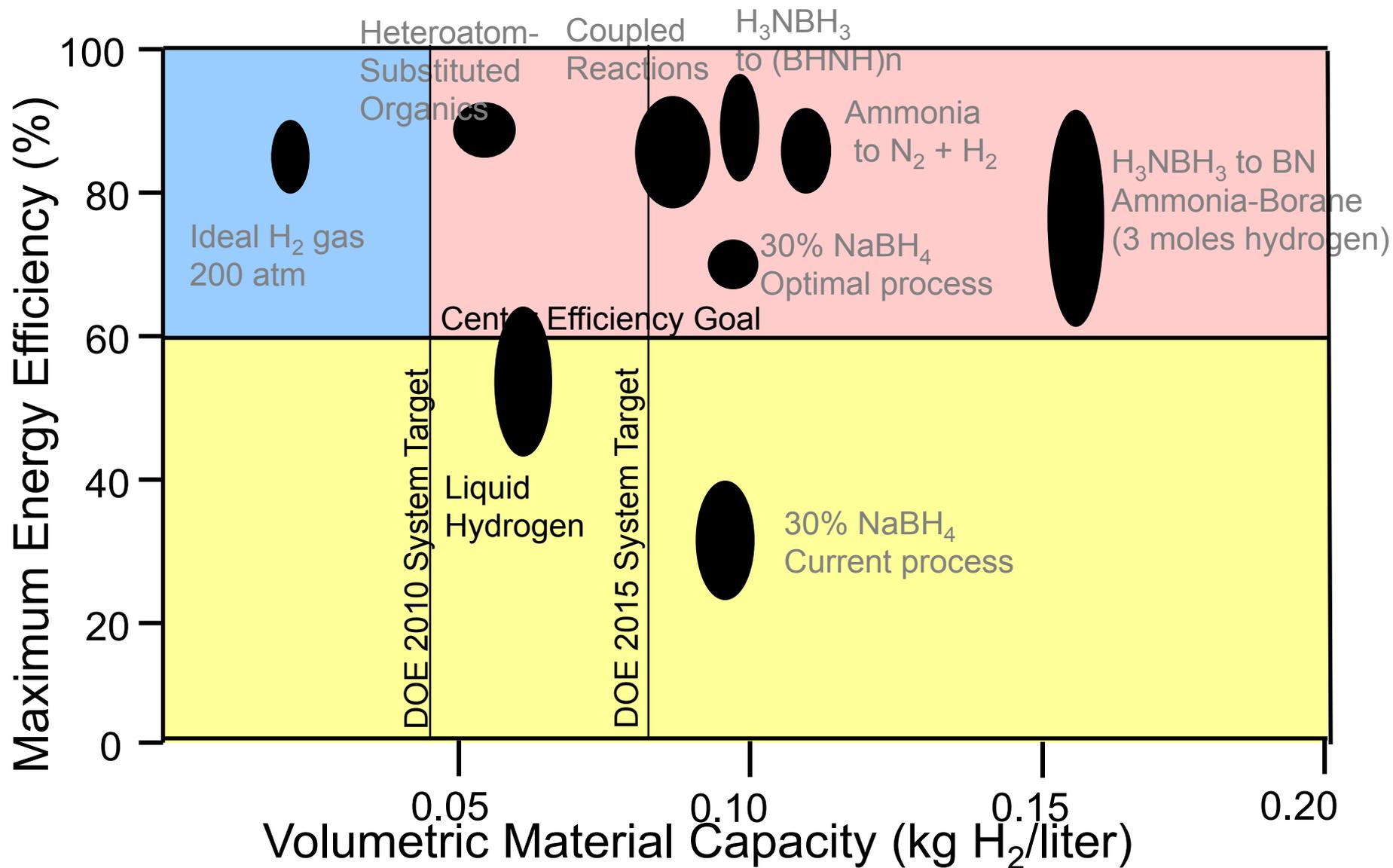
- AB release is too exothermic to reverse with hydrogen pressure
- Must resort to off-board chemical processes to convert spent fuel back to AB
- Must be chemically and energy efficient

2006 – began to consider 'boundary conditions' for chemical regeneration of any hydrogen storage material



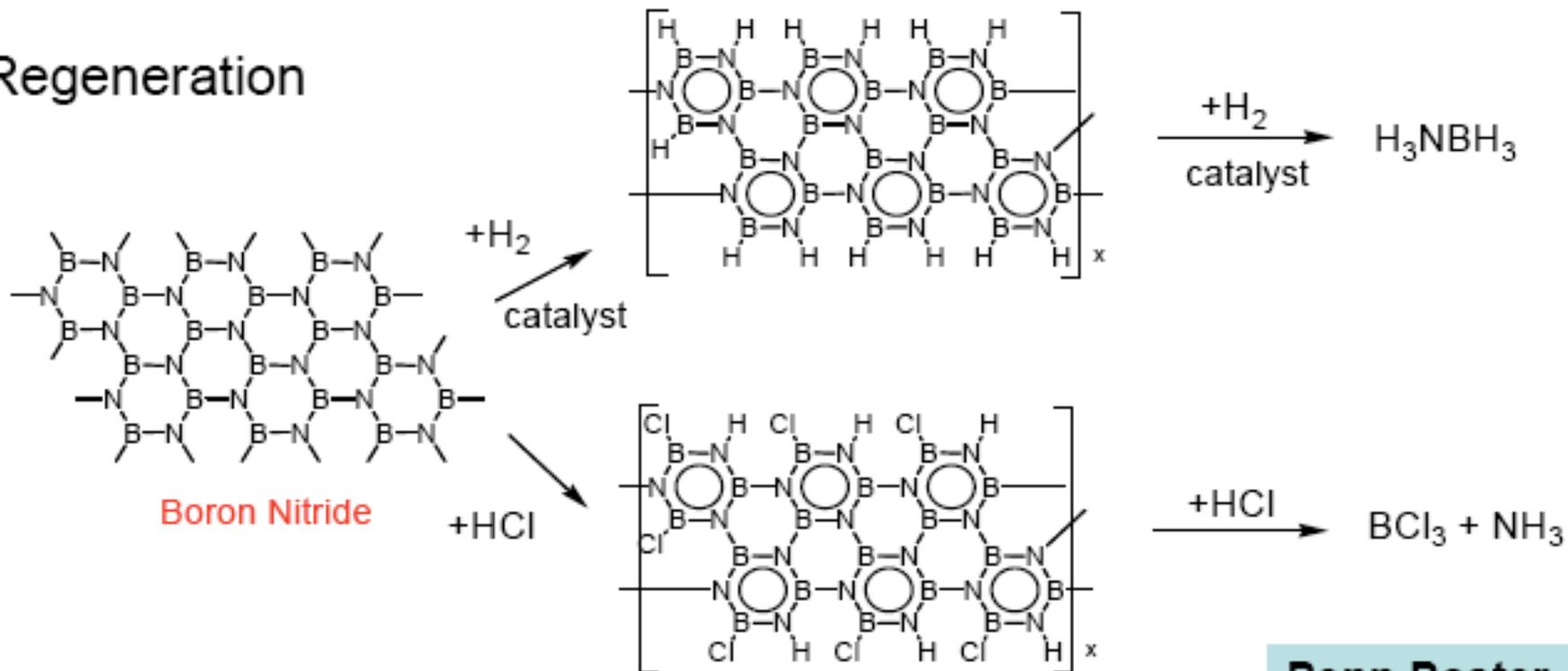
2005: Relative Ideal Efficiencies of Regeneration

AB continues to have promise for storage



Regeneration Ideas – State of the Art 2005

Regeneration



Penn Poster

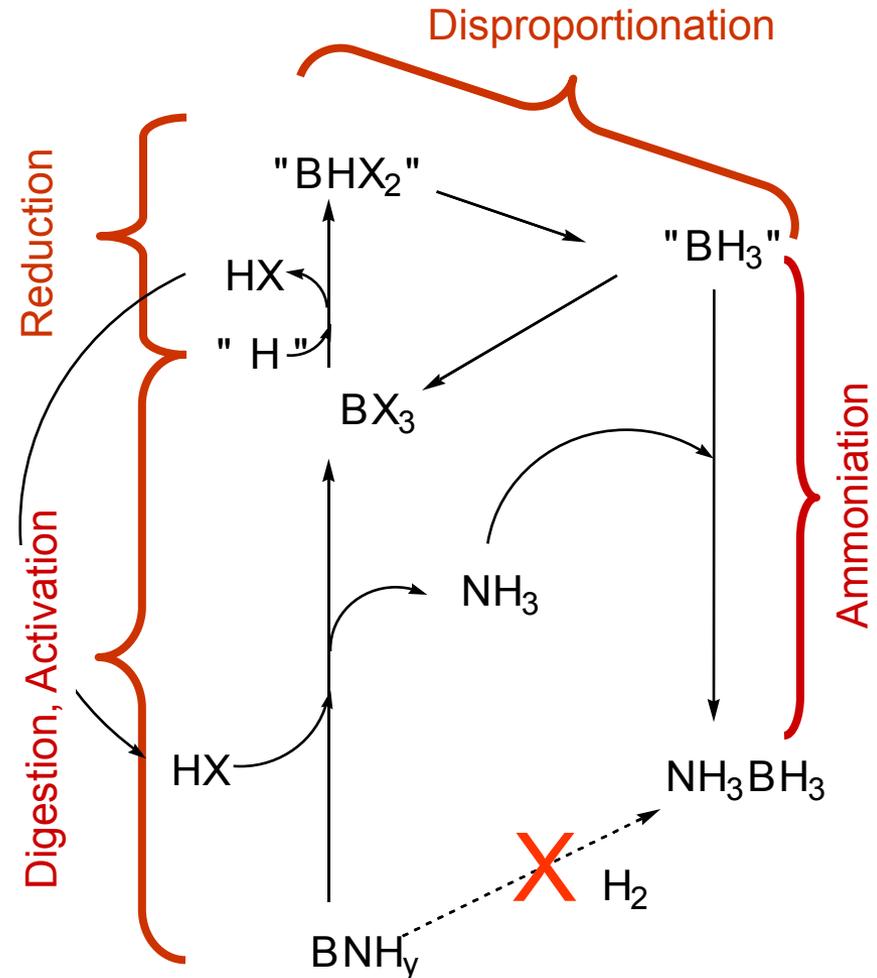
2006: Toward Regeneration of Ammonia Borane

APPROACH (LANL/Penn)

- **Digest spent material without wasting remaining B-H bonds**
- Use lowest-energy, least expensive reductant possible
- **Use thermoneutral or reversible steps wherever possible**
- Find high yield reactions

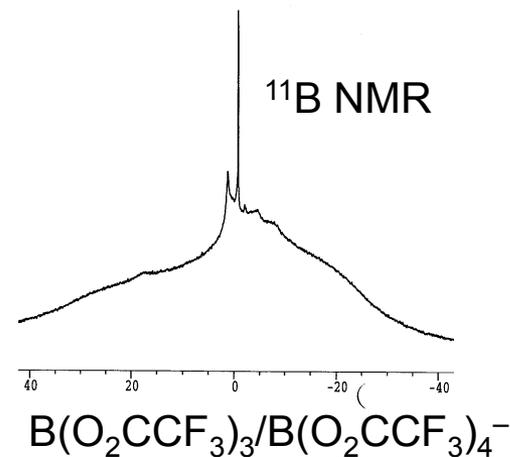
RESULTS

- Developed 5 step concept
- Demonstrated 3 of 5 steps in lab
- Demonstrated regenerable hydride
- Identified other hydrides for reduction step

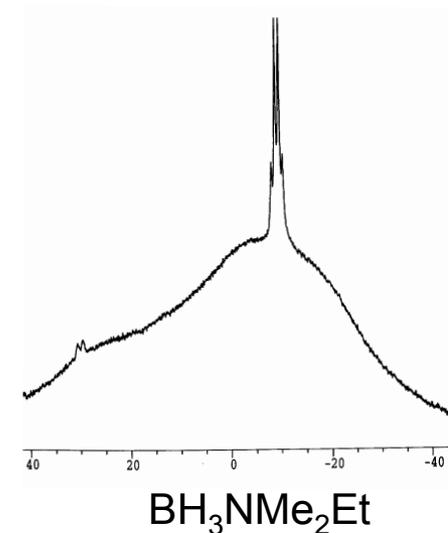
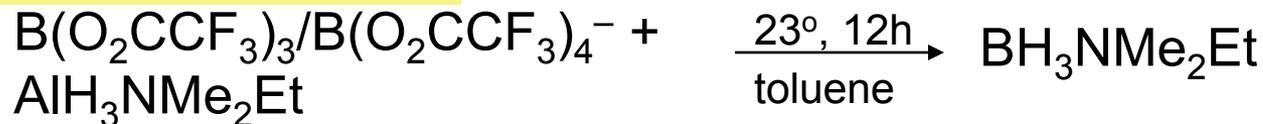


2006: Initial Penn Regeneration Method Employed Strong Organic Acids

Digestion



Reduction to Borane

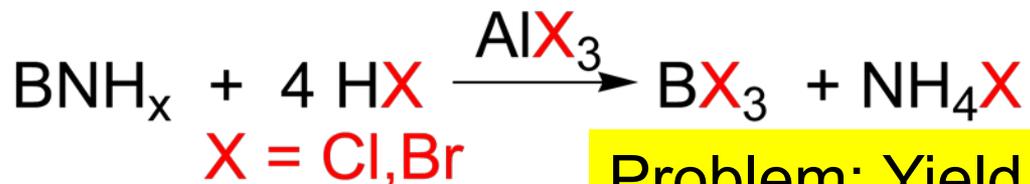


Major Problems

- Trifluoroacetic acid is expensive and difficult to handle
- Ammonia is not recovered
- The reduction of B-O bonds requires a strong (and expensive!) reducing agent

2007: New Penn Regeneration Process Avoids The Formation of B-O Bonds

First Step: Digestion of Spent Fuel by Super Acidic Halo-Acids



Problem: Yield in first step low, unreactive byproduct formed

Second Step: One-Pot Conversion of BX_3 to AB

Amine-Coordination of BX_3



BX Reduction

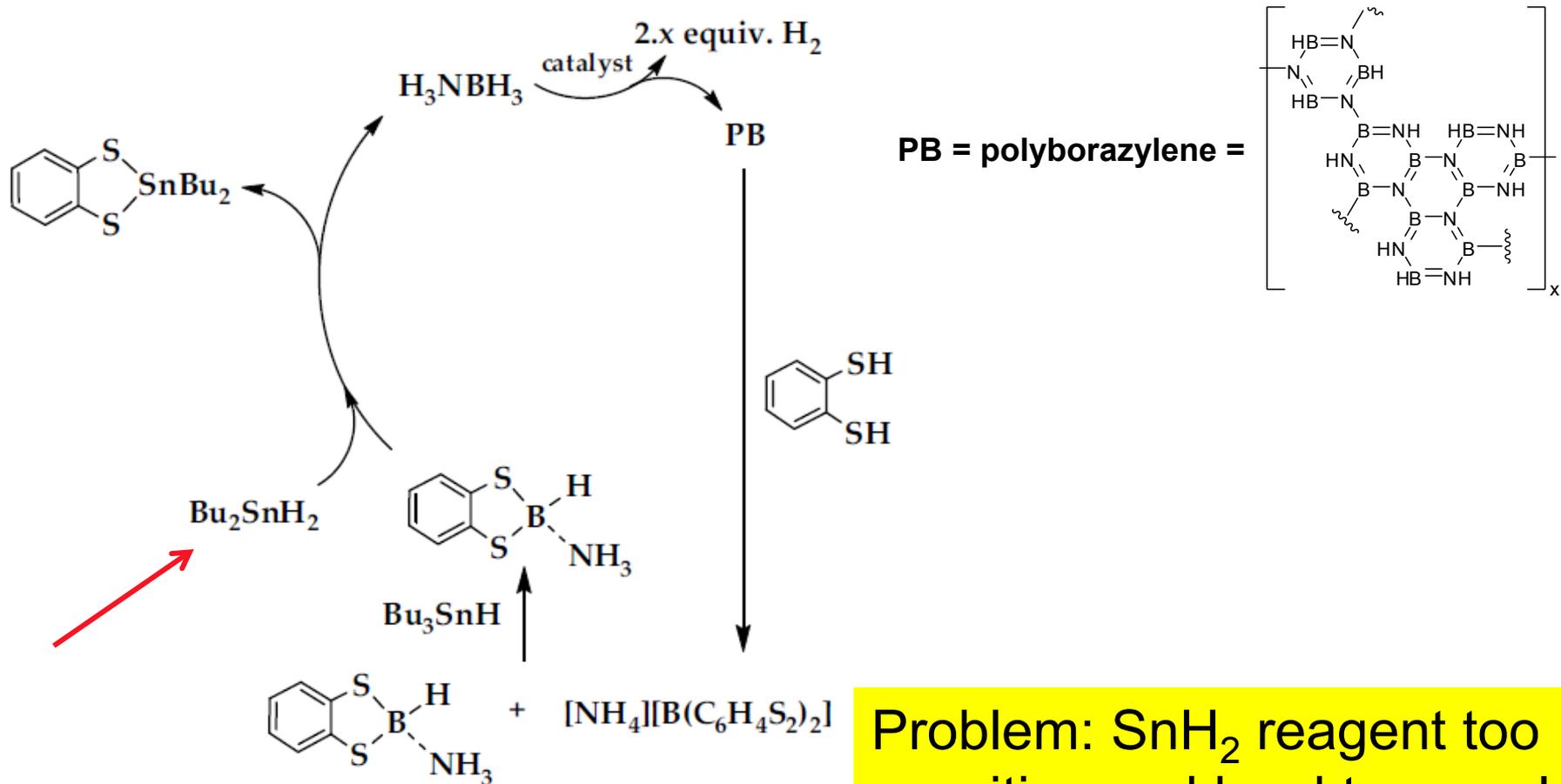


Amine Displacement by NH_3 Yields AB

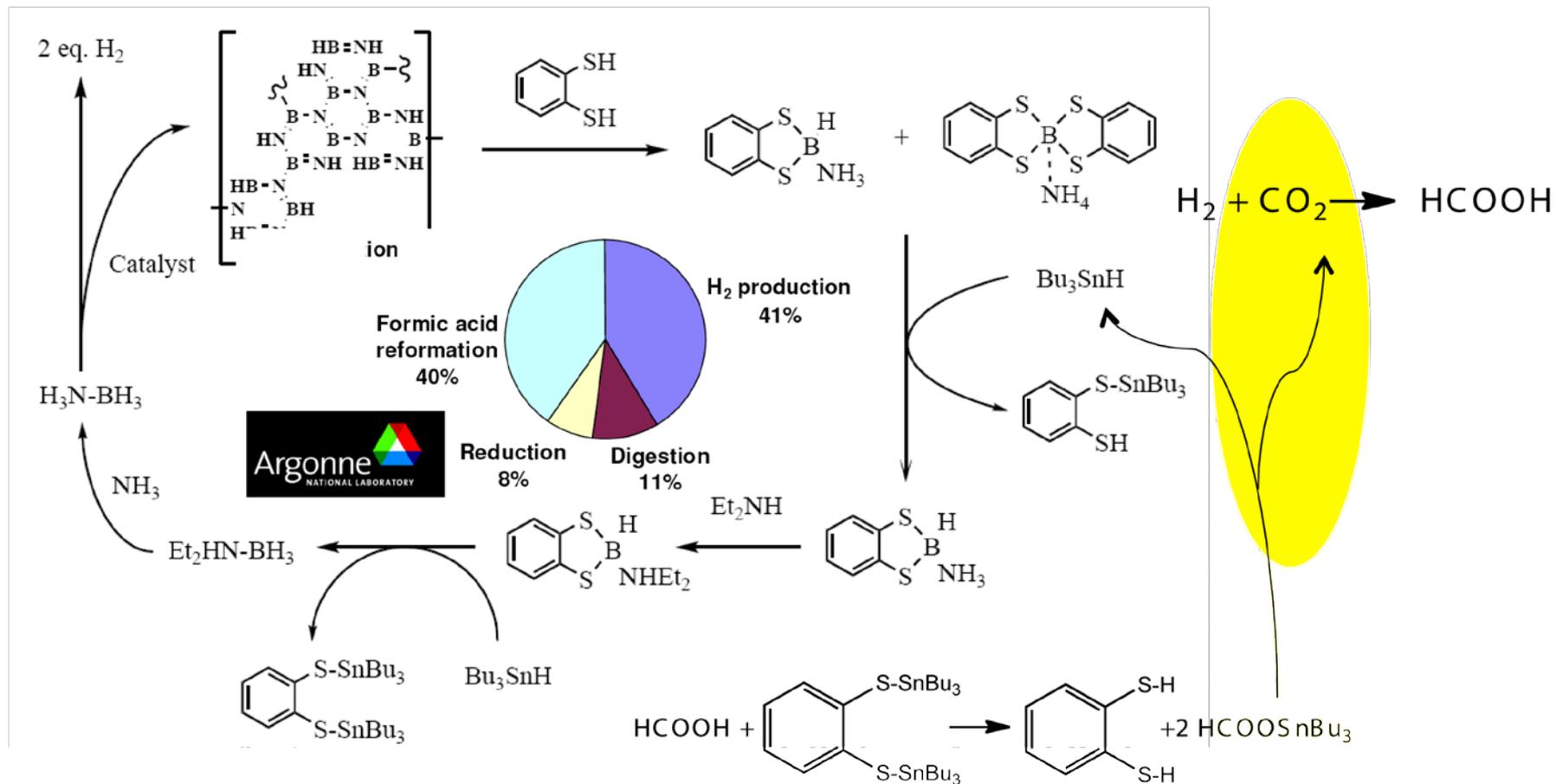


Complete Regen Cycle 3

LANL AMR 2007

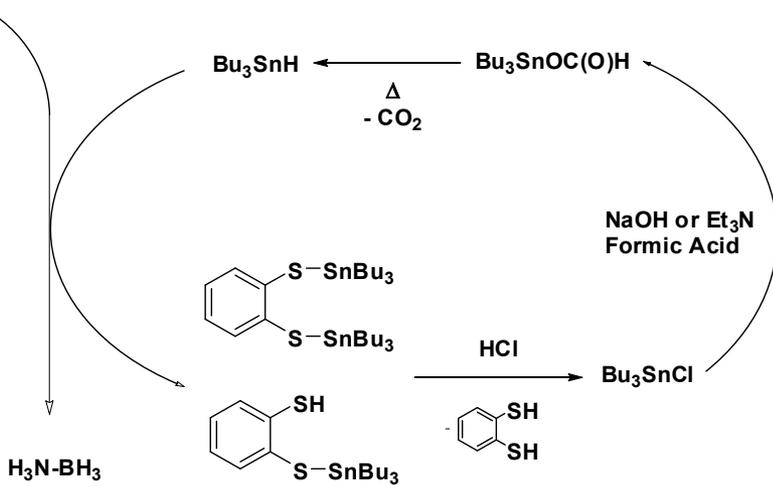
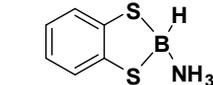
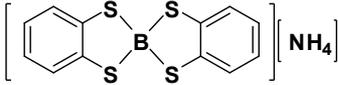


Complete Regen Cycle 4: LANL AMR 2008: Formic Acid as Hydrogen Transfer Reagent

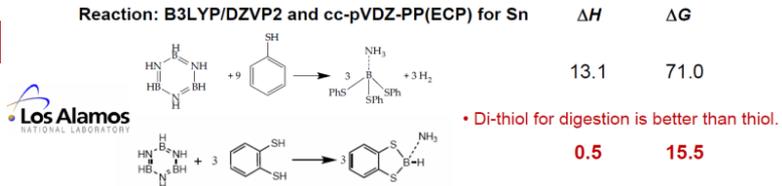


Problem: Subsequent analysis by ANL determines that CO₂ compression for formic acid recycle too energy intensive -- DISCONTINUED

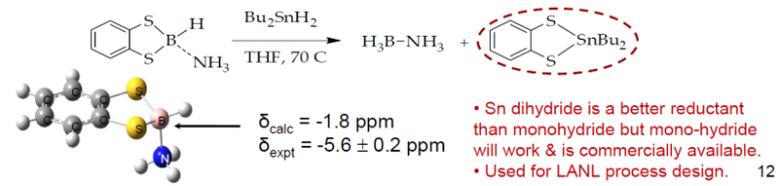
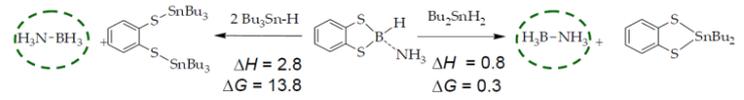
Complete Regen Cycle 4a Improvements Guided by Theory: UC Davis, Alabama, LANL AMR 2009



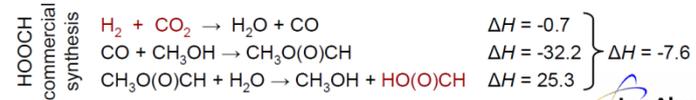
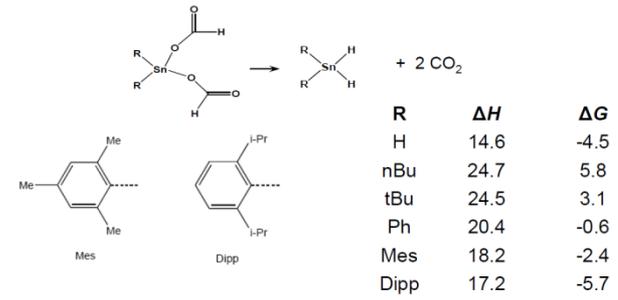
Alternatives to Digestion: S and Sn Compounds (298K)



Reduction



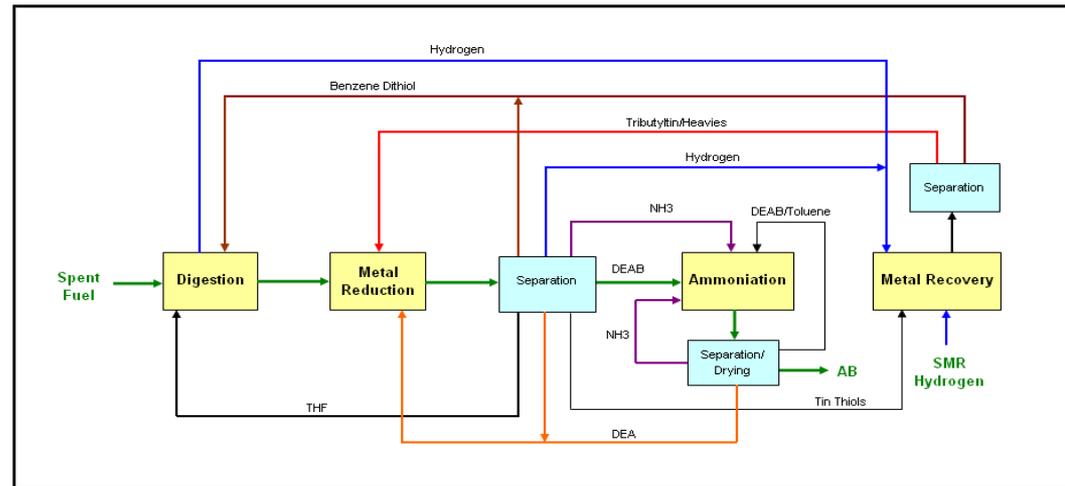
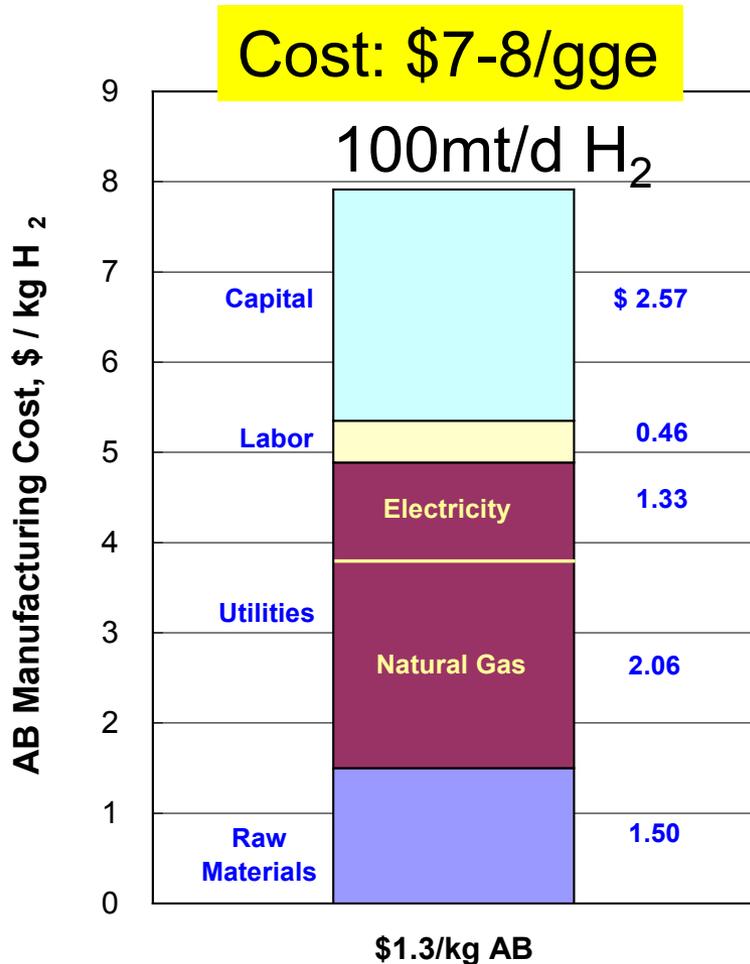
Dihydride Recycle CO₂ extrusion from tin diformates at 298 K in kcal/mol



• CO₂ extrusion chemistry favored for free energy due to loss of CO₂.
 • Issue is inefficiency of formic acid recycle. Work with LANL to improve the process. 14

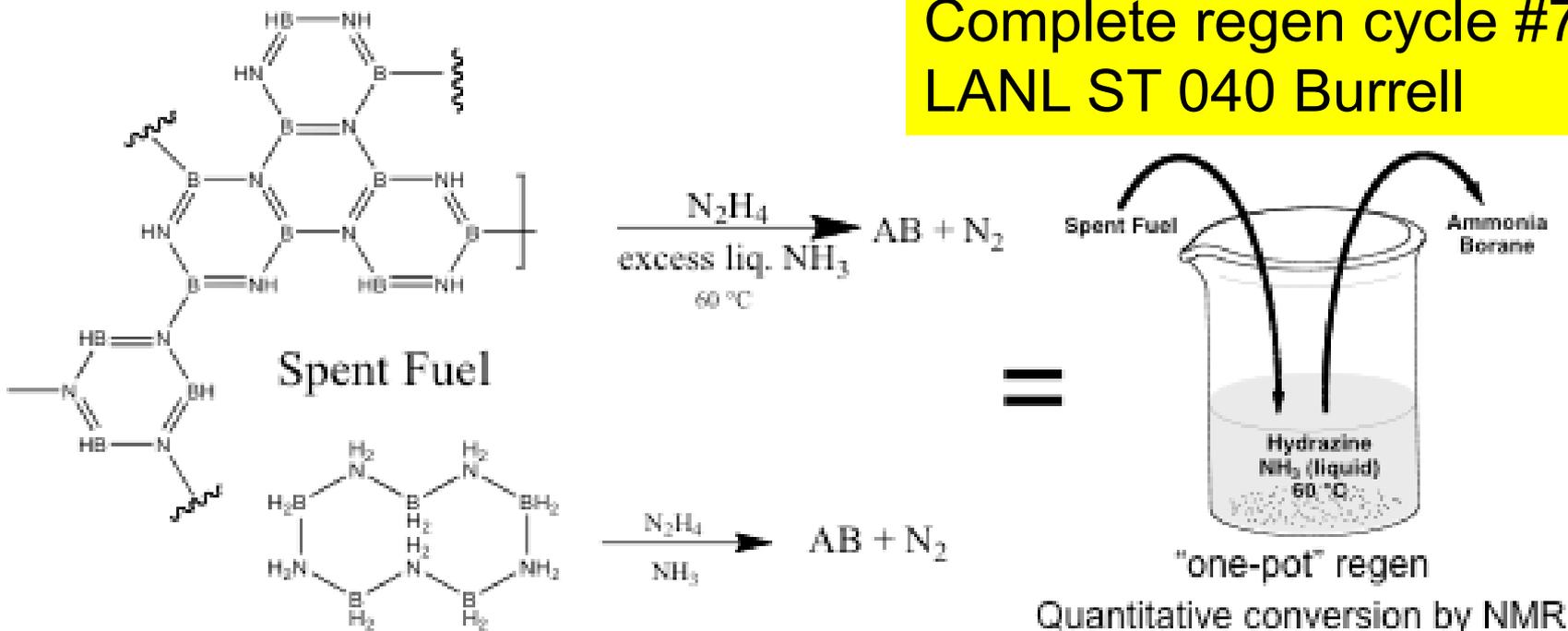
2009: Path forward identified to reducing regeneration costs from \$7-8/gge

- Complexity, separations leads to high capital and operating costs
- Mass of materials being moved through process are also major contributors to cost



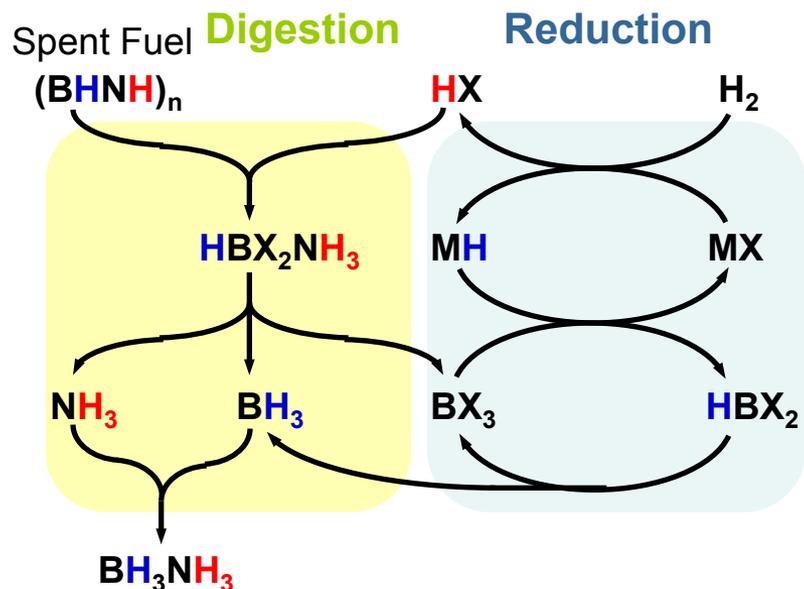
Current Progress in Spent Fuel Regeneration: Simplified, 'One Pot' Regeneration of AB

Complete regen cycle #7
LANL ST 040 Burrell

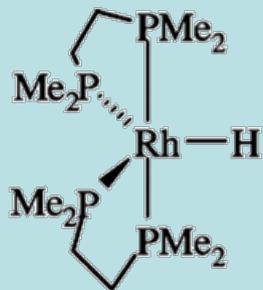


- This method works for **multiple spent fuel** forms *including spent fuels from ionic liquids* giving ammonia borane.
- Much lower mass throughput relative to previous process should lead to **improvements in process efficiency and capital cost. Current hydrazine cost an issue.**

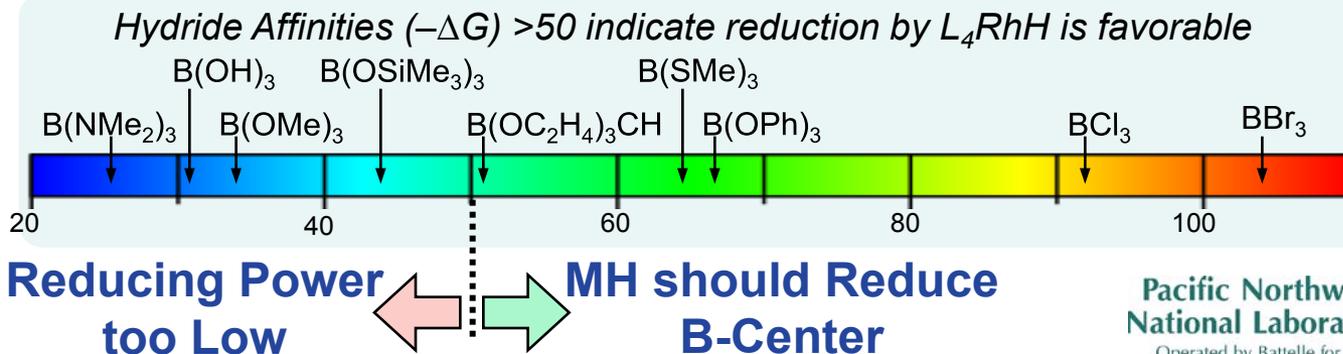
2007-2010 PNNL Scheme for AB Regeneration: Different Approach --Search for Direct H₂ Transfer



- Scheme under development to use H₂ as hydrogen source for regeneration
- Need to match properties of digestion agent and reducing agent to minimize energy associated with regeneration
- Hydride transfer reactions using this scheme now demonstrated using phenol followed by L₄RhH
- Not able to complete the cycle at this point in time

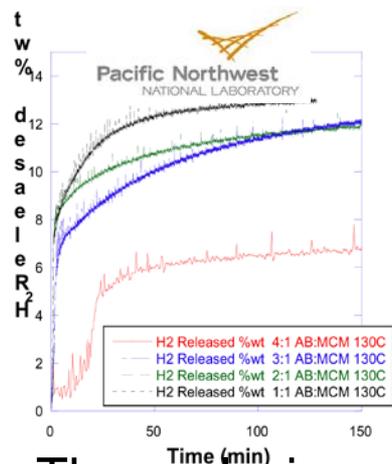


Weak MH Bonds
are Good
Potential Donors

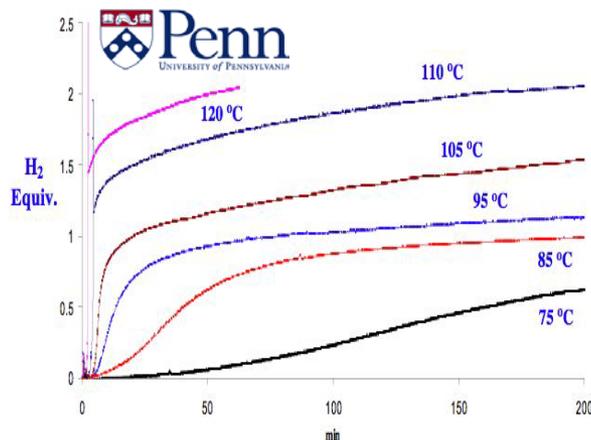


Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Summary: Three distinct pathways to achieve high hydrogen release rates and capacity

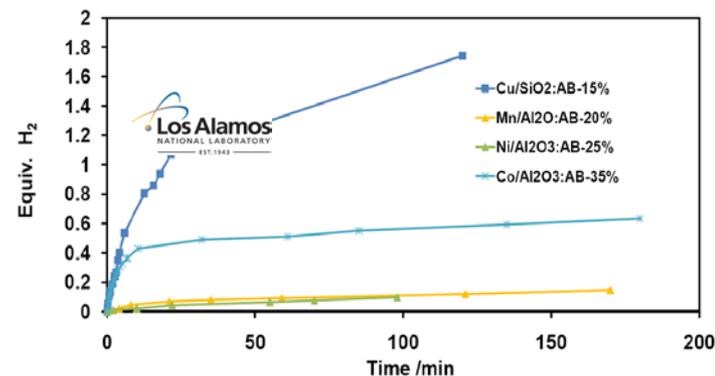


- **Thermolysis**
 - Solid fuel systems
 - Foaming - solved
 - 2nd mole release rate lower
 - Additives enhance rate, influence impurities



- **Chemical Initiators**
 - Ionic liquids initiate dehydropolymerization
 - Potentially fluid fuel
 - Very fast release rates at moderate temperature
 - Proton sponge additive increases rates, decreases impurities

Base Metal Dehydrogenation of AB at 70°C



- **Catalytic Release**
 - Requires liquid fuel
 - Reaction control simpler
 - 2nd mole release rate lower
 - ‘Solvents’ reduce wt. % H₂
 - Need H₂ donor ‘solvents’ to mitigate losses in capacity, or high concentrations in ILs
 - Reduced impurities

Current state: Engineering considerations favor liquid fuels. Innovation in onboard solids handling still required to enable AB, AlH₃, LiAlH₄ systems

Accomplishments

Status of Center's Approach to Meet Technical Barriers

- Gravimetric (Center criterion > 7 wt. %)
 - Ammonia borane (AB):
 - solid >13 wt. % 130 °C
 - in ionic liquids $7 - 11$ wt. % < 110 °C
 - Metal amidoboranes
 - Solids $7 - 13$ wt. % < 130 °C
 - No path forward to regen at present
 - Cyclo CBN compounds – potentially reversible; liquids, solids $5 - 7$ wt. %
- Volume - all of the above compounds or mixtures are likely to exceed $.045$ kg H_2 /liter = DOE target
- H_2 release kinetics - demonstrated release rates from 70 °C – 110 °C that have potential to exceed the target
- Regeneration: Off board processes
 - Demonstrated 7 complete cycles
 - One pot regen with hydrazine!
- Energy efficiency analyses
 - Argonne has provided analyses for 4 CHSCoE regen processes
 - Steady improvements in energy efficiency
 - Started mid 'teens, now mid 30's (ANL)
 - ANL conducting onboard analysis of AB/IL liquid release
- Cost – R&H/Dow has completed:
 - First fill of AB from SBH analysis $\$9$ /kg
 - Cost of 1st regen process: $\$7-8$ /kg
- System life-cycle assessments
 - US Borax provided updated borax resource analysis indicating ample US resource

Path Forward for Chemical Hydrogen Storage

- Develop materials for short term, stationary applications as stepping stones to the more demanding problem of onboard storage
- Cost of hydrazine an issue for current favored regen process
 - New approaches to synthesis required
- Off board regen will always be more costly, less efficient than direct onboard rehydrogenation
 - Search for systems with near thermoneutral release to ease onboard heat rejection requirements
 - Take advantage of rapid release from slightly exothermic materials with potential for onboard, direct regeneration
- Liquid systems with high recyclability must be demonstrated
 - Most readily engineered to a storage system
 - IL stability, longevity critical element moving forward
- Innovations in solids handling required if offboard regenerable, solid release materials are to meet transportation targets
 - AB, LiAlH_4 , AlH_3 , complex 'metal hydrides', etc.

Key Contributions of the CHSCoE

- 5 years ago:
 - Release from high capacity amine boranes known, but too slow
 - No known route to regenerate spent fuel
 - Inefficient synthesis of SBH
 - Influence of boron-based storage on borate reserves not defined
 - Solid systems only – and no known onboard solid handling schemes
 - No liquid fuels known for borane systems
- Current state:
 - Catalytic and thermal release rates that can meet or exceed DOE targets at $T < 110\text{ }^{\circ}\text{C}$
 - Several chemical regeneration schemes demonstrated
 - Preliminary cost analysis (\$7-8/kg H_2)
 - Regen with hydrazine scheme markedly simpler, potentially less expensive (with improvements in N_2H_4 cost)
 - Potentially liquid systems identified
 - Solid handling concepts for onboard release systems remain a technical challenge

The Center Approach

- Center milestones and down selects helped to keep research focused and moving ahead efficiently
- Communicated safety issues rapidly
- IP agreement allowed rapid and effective communication
- Catalyzed technical brainstorming and progress
- Allowed sharing of both intellectual and physical capabilities
- Encouraged breadth in developing international partnerships and collaborations
- Peer to peer friendly competition encouraged rapid progress

Thanks! To those who helped organize the Center, and the too-numerous-to-note scientific contributors

- Grace Ordaz, Office of Hydrogen and Fuel Cells Technology
- Chris Aardahl, PNNL
- Jamie Holliday, PNNL
- Tony Burrell, LANL
- And to those that developed the Center and got it off to a running start:
 - Bill Tumas, LANL, now NREL
 - Moe Khaleel, PNNL
 - Dave Thorn, LANL
- All of our partners and collaborators, past and present