

PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence

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Overview

Timeline

- Start 3/2005
- End 3/2010
- 60% Complete

Budget

- FY07: \$1700K
- FY08: \$2050K

Barriers Addressed

- Volumetric Density
- Gravimetric Density
- Hydrogen Release Rate
- Fuel Cost
- Fuel Cycle Energy Efficiency

Center Collaborations



Project Objectives

Center

- **Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets**
- **Develop high efficiency off-board methods for chemical hydride regeneration**

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- **Meet Center objectives through studies and development of high capacity chemical hydrides (NH_3BH_3 (& isomers), NH_4BH_4 , B-N/M-H hybrids)**
 - **Increase kinetics while maintaining high capacity**
 - **Hybrid materials to control thermodynamics**
 - **Controlling morphology: materials engineering**
 - **Regeneration of NH_3BH_3 : matching digestion and reduction**

Specific Approach for this Review Period

- Increase rate for the second equivalent of hydrogen release from NH_3BH_3 or related systems to achieve rate target
- Develop methods to control morphology of NH_3BH_3 during H_2 release to enable solids handling
- Develop experimental program to explore use of 'activated' H_2 as a means to regenerate spent B-N fuels to reduce fuel cycle costs
- Use theory to guide matching of digestion and reduction chemistry in regeneration schemes
- Develop preliminary flow sheets for PNNL regeneration scheme to identify knowledge gaps
- Examine hybrid materials based on BH_3NH_3 and LiH/NaH to explore a new class of materials
- Quantify H_2 impurities from the B-N and B-N-X systems to understand potential impacts on fuel cell operation

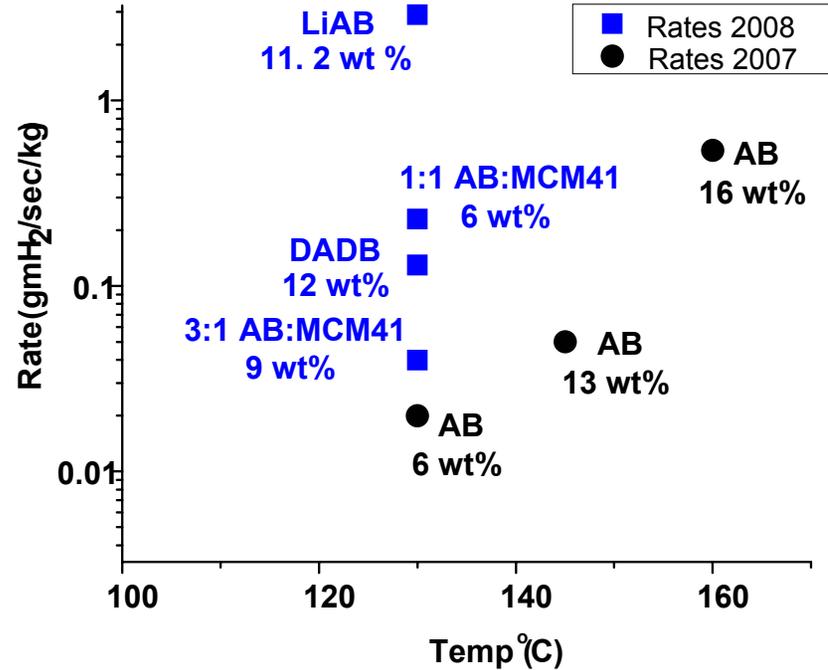
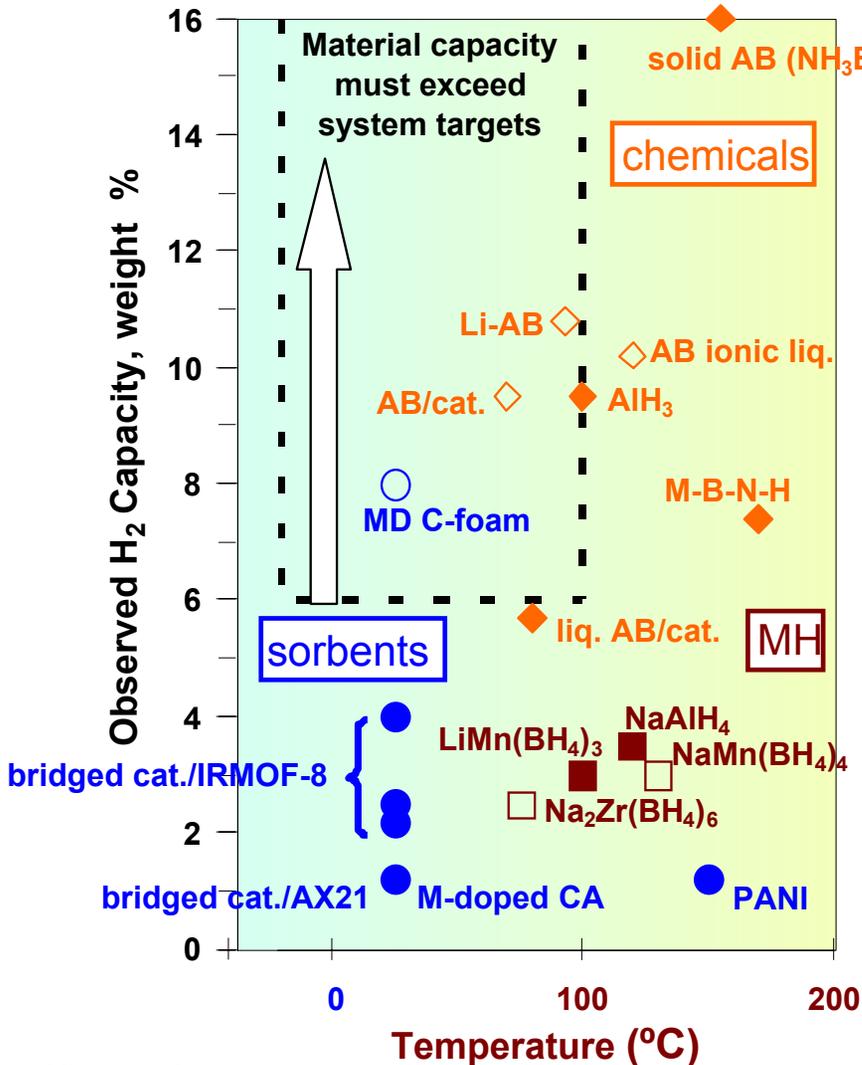
Major Achievements for the Review Period

- **Developed Li-NH₂-BH₃ under IPHE collaboration: worth additional pursuit: H₂ release kinetics increased by order of magnitude**
- **Discovered additives that suppress foaming of NH₃BH₃: enables pursuit of engineered system**
- **Demonstrated hydride transfer chemistry from 'activated' H₂ to spent fuel: confirms theory results from 2007 AMR**
- **Theoretical calculations now point to energy efficient regeneration approach with non-PGM reduction pathway: reduced fuel cycle costs**
- **Preliminary flow sheets for regeneration enables identification of process knowledge gaps**

Milestones – FY 2008

Q4		Complete characterization of mechanism for second equivalent of hydrogen from ammonia borane. Deliver research direction for development of additives to accelerate release of second equivalent without destabilization of the fuel.
Q3		Quantify the purity of hydrogen released thermally from ammonia borane as a function of temperature. Understand gap between observed data and 2010 target.
Q2		Finish characterization of alternative ammonia borane-scaffold materials and quantify thermochemistry. Quantify kinetics and thermodynamics. Deliver assessment versus 2010 targets and neat ammonia borane.
Q4		Demonstrate bench scale regeneration at 40% energy efficiency (Center milestone with LANL, Penn, UC Davis).
Q3		Complete characterization of mechanism for foaming during hydrogen release from ammonia borane solids. Deliver research direction and list of options for mitigation of foaming.
Q4		Complete the characterization (NMR, TGA/DSC) of the LiH/AB system and assess capacity and reversibility
Q4		Submit a minimum of 1 joint publication from the IPHE activities with the UK, Singapore, New Zealand, and the US
Q2		Complete down-selection process for 2010 engineering & 2015 science in collaboration with the entire Center

Progress on Hydrogen Release (2008 vs. 2007)



- Order of magnitude increase in release rates
- ABH₂ kinetics too fast to measure with existing methods

PNNL: Karkamkar, Choi, Daschbach, Autrey

Modified from Thomas & Sandrock, DOE

Summary Table

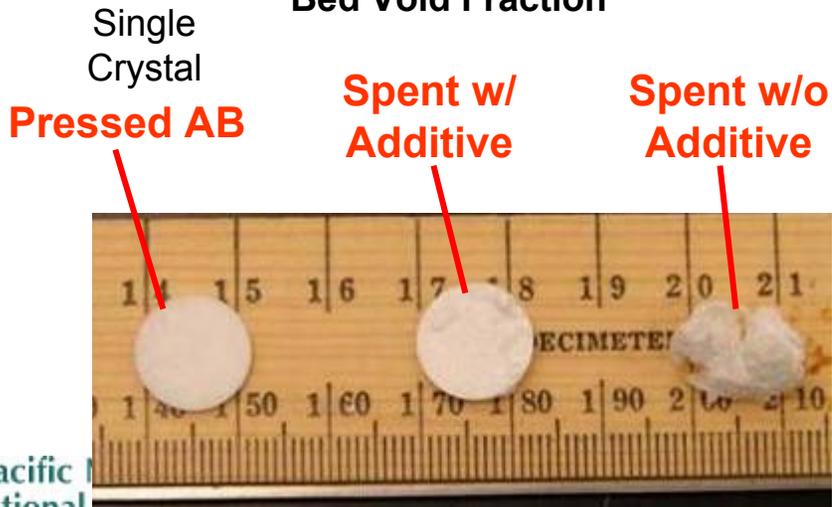
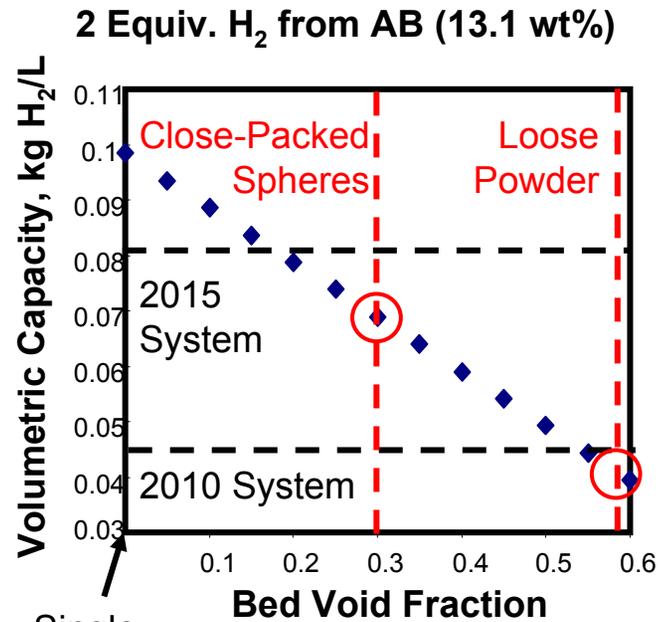
2007 – Neat AB (per kg on rates)

	1 eq H ₂	1.5 eq H ₂	2 eq H ₂	2.5 eq H ₂	Peak rate
160°C	50 sec (1.3 g/s)	80 sec (1.2 g/s)	240 sec (.54 g/s)	1000 sec (.16 g/s)	3.8 g/s
145°C	70 sec (.93 g/s)	200 sec (.5 g.s)	1200 sec (.11 g/s)		2.1 g/s
130°C	150sec (.43 g/s)	1000sec (.1 g/s)			1.1 g/s

2008 – AB Derivatives

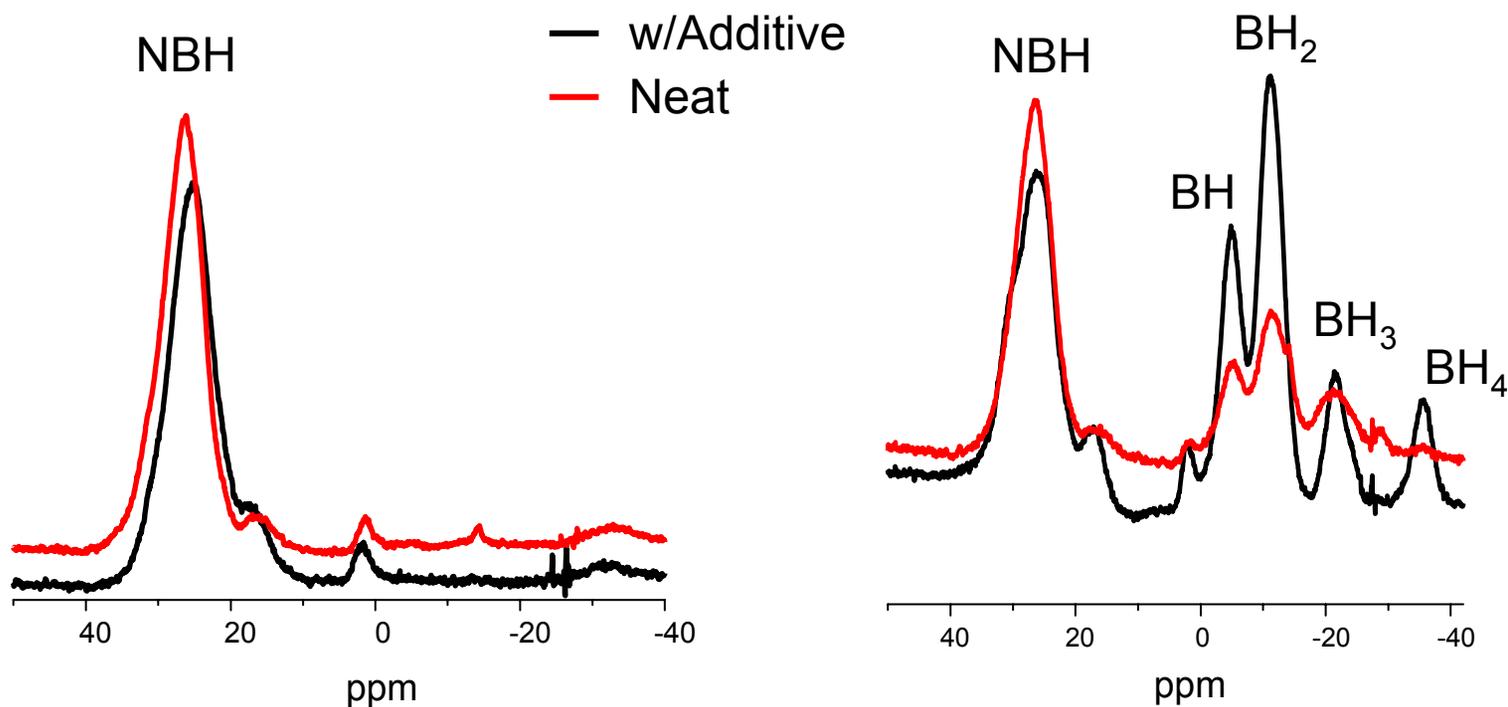
	Wt %	Temp (°C)	2 Eq. Avg. Rate (130°C; g/s/kg)	Foam?
Li-AB	11.2	< 100	2.9	NO
ABH ₂	12.2 - 21.4	40 - 130	VERY FAST	NO
DADB	12	90 - 130	0.13	NO

Additive Discovered Allows High Volumetric Density & Prospect of an Engineered System for Solid AB



- System targets are difficult for granulated materials
- Addition of a spent fuel tank cuts the volumetric density in half
 - AB foams when it releases hydrogen – not conducive to engineering
 - Potential show stopper
- Campaign on anti-foaming initiated in Q1, FY08
 - More than 50 additive formulations tested with 2-3 successful (Patent Filed)
 - Scaffold materials also demonstrate foam suppression at lower AB:scaffold loadings
 - Paves the way to systems with monolithic fuels & high volumetric density

^{11}B NMR: No Evidence of Reaction Between AB & Additive

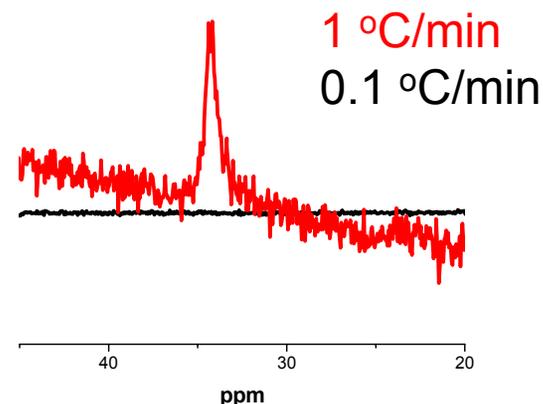


155°C: 2 – 2.2 Eq. H₂

120°C: 1.3 Eq. H₂

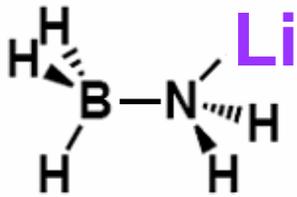
Measurements of Volatile Impurities Show Small Amounts of Borazine and NH_3

- Pass H_2 through THF to trap borazine \rightarrow measure via NMR
 - 1 °C/min (detected)
 - 0.1 °C/min (not detected)
- Daigger tube (Kitagawa)
 - Measure $[\text{NH}_3]$ in H_2 from gas burette
 - Isothermal (120 °C; 1.3 eq H_2): NH_3 ca. 170 ± 10 ppm
 - Unclear whether a decomposition product or residual from synthesis
- Impurities at low levels can be handled through filtration or reactor design approaches

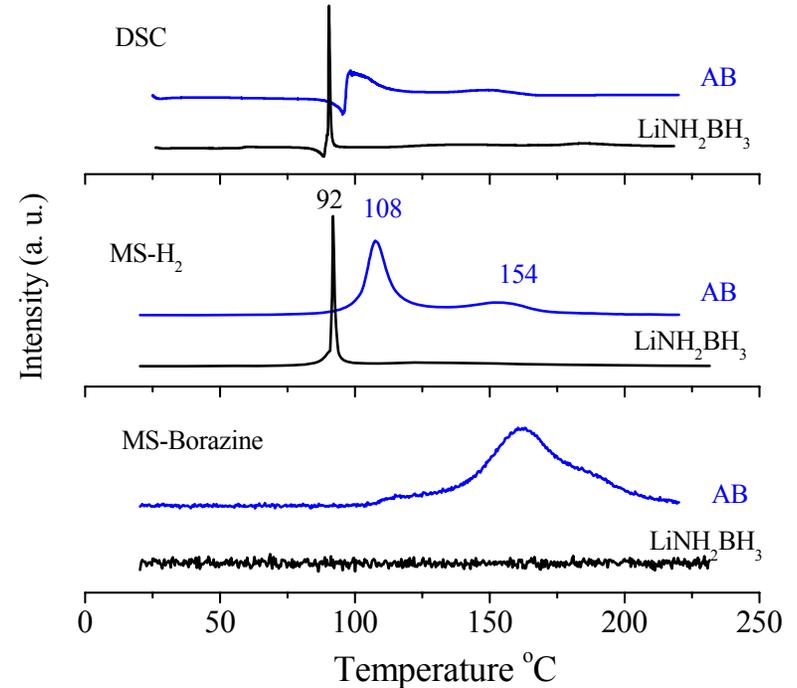
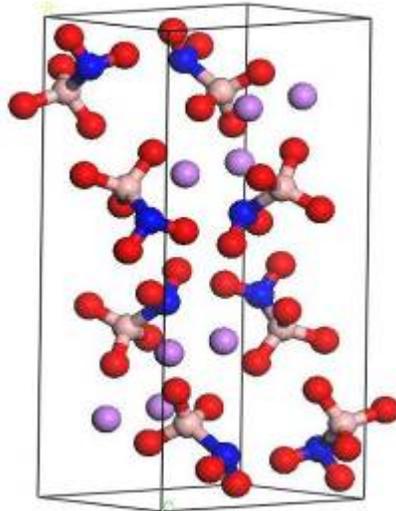


Li-AB: Fast Kinetics & Little Barrier on Second Equivalent of H₂ (all release < 100°C)

- Material mixtures allow engineering thermodynamics and kinetics
- Demonstrated release of 2 equivalents (~11 wt%) of hydrogen below 100°C; release of 2nd equivalent is very fast compared to AB
- No borazine impurity in the hydrogen released
- Faster kinetics for a given wt% than neat ammonia borane



Red – H
Blue – N
Pink – B
Purple – Li



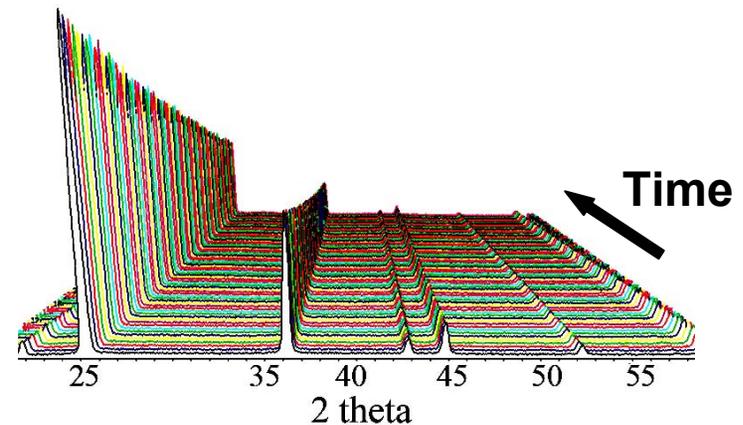
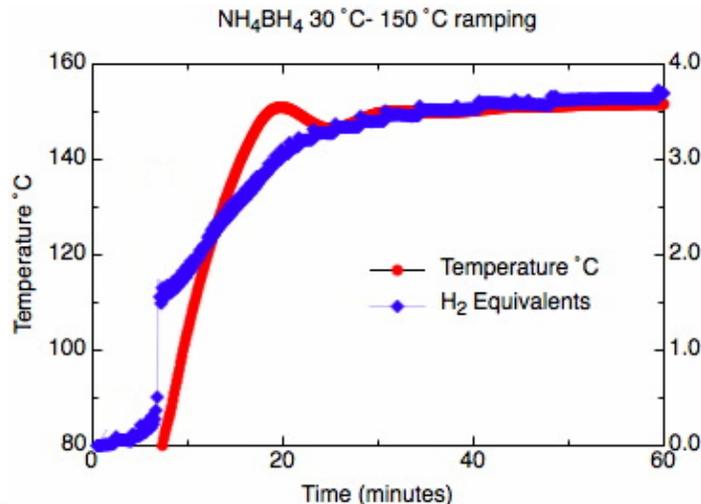
PNNL: Autrey, Shaw, Karkamkar

NUS: P. Chen; **RAL:** W. David; **Oxford:** P. Edwards

Xiong et al. (2008) *Nature Materials* 7, 138.

Ammonium Borohydride Has Potential

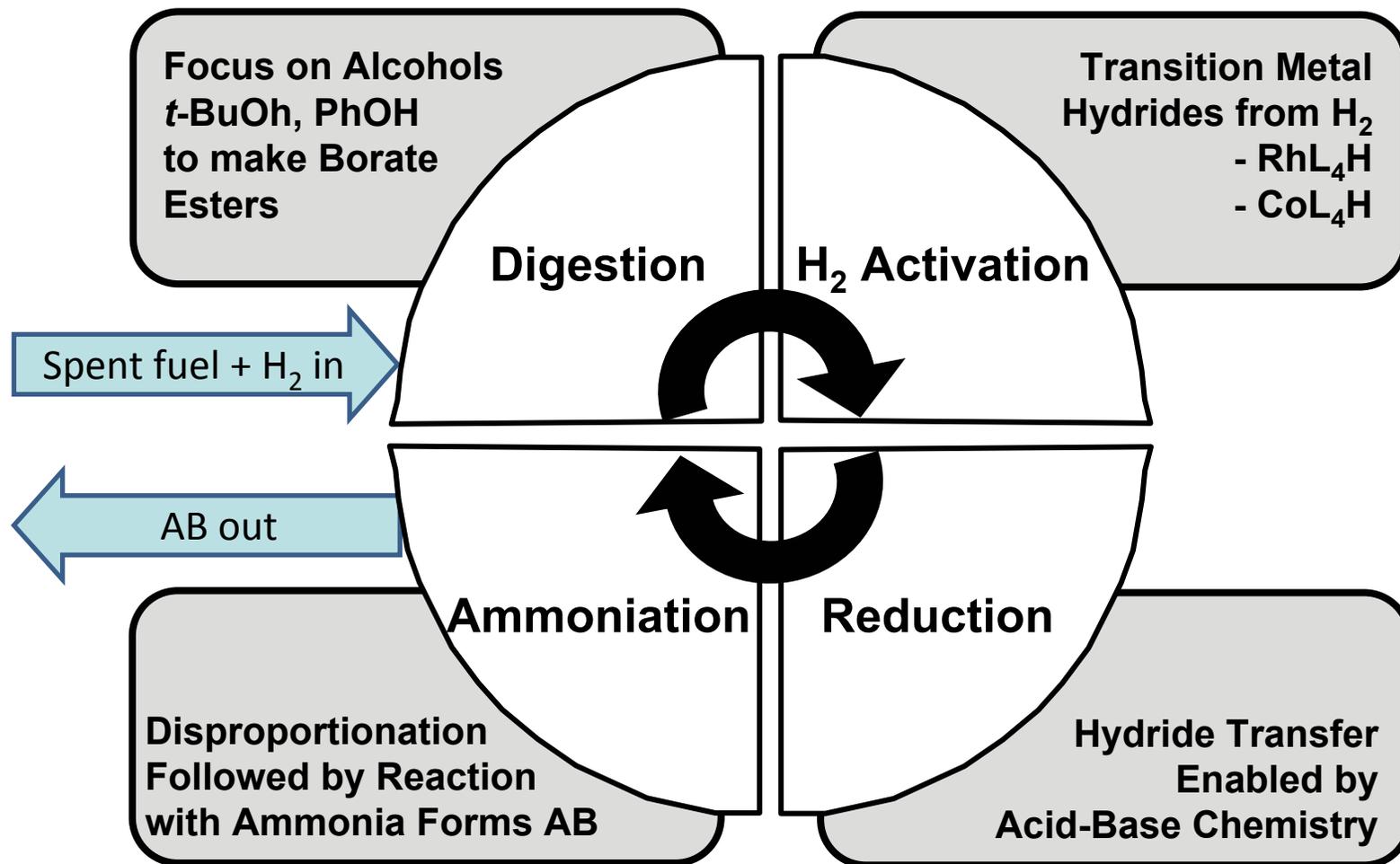
- Fast kinetics for 12 wt%
- Literature indicates compound not stable: PNNL has demonstrated that stability enhancement possible with careful synthetic approaches
 - More stable than previously reported: stable at -30°C
 - Opens up opportunities to look at materials based on ABH_2
- Step 1: $\text{ABH}_2 \rightarrow \text{AB} + \text{H}_2$
- Step 2: $\text{ABH}_2 + \text{AB} \rightarrow \text{DADB} \rightarrow \text{PAB} + \text{H}_2$
- Complete reaction (150°C): 20 wt% H_2



XRD of ABH_2 : $t_{1/2} = 16\text{hrs}$ under ambient

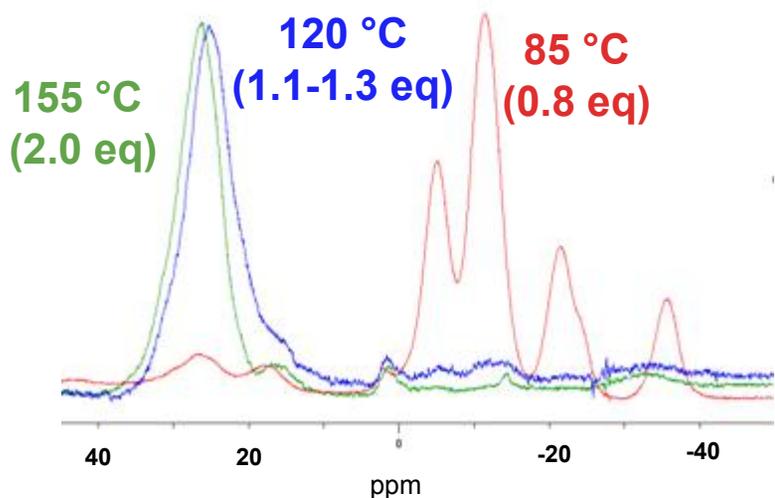
PNNL: Karkamkar, Heldebrant, Autrey

Proposed at 2007 AMR: Regeneration of AB with 'Activated' H₂

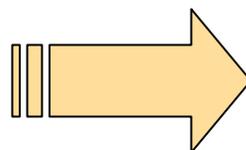


NMR Characterization Key to Confirming Efficient Regeneration Chemistry

Solid ^{11}B : 800 MHz

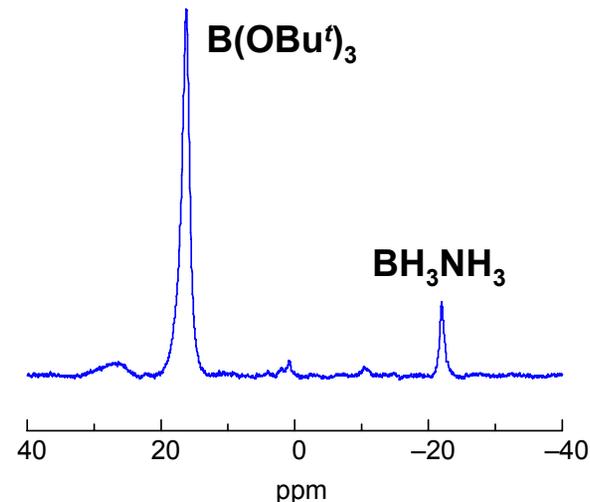


$t\text{-BuOH}$



NH_3

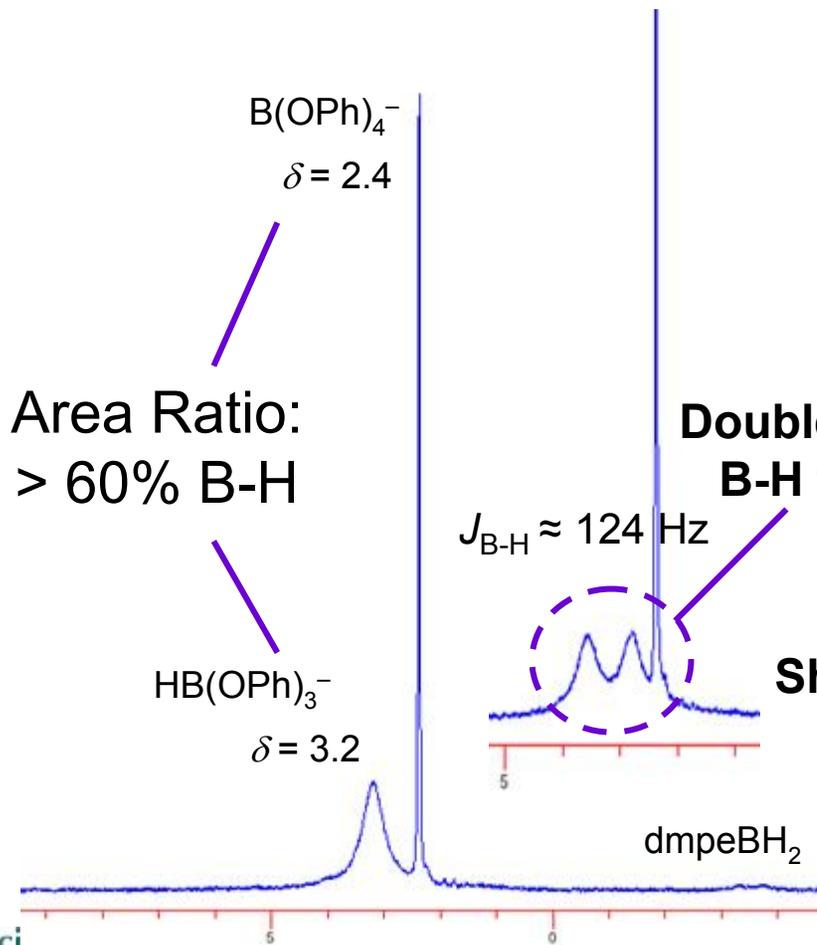
Solution ^{11}B : 300 MHz



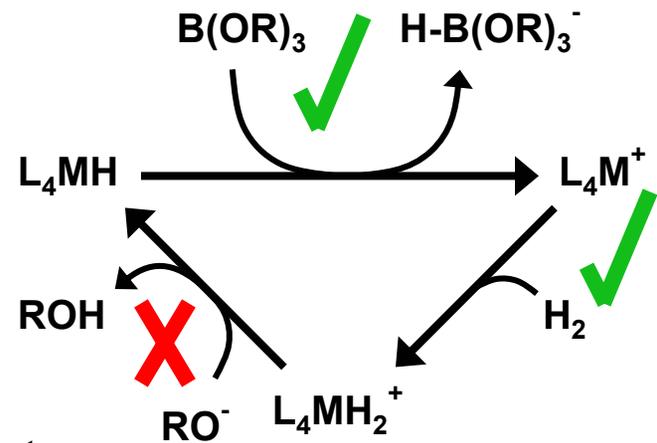
- ≥ 2 eq H_2 gives polyborazylene-like products
- Polyborazylene undergoes digestion relatively easily
- Spent fuel characterization complete
- Digestion pathways in good shape
- Principle focus in FY08 on reduction chemistry

NMR confirms $(dmpe)_2RhH$ can reduce $B(OPh)_3$: Points to Efficient Pathway for Regeneration

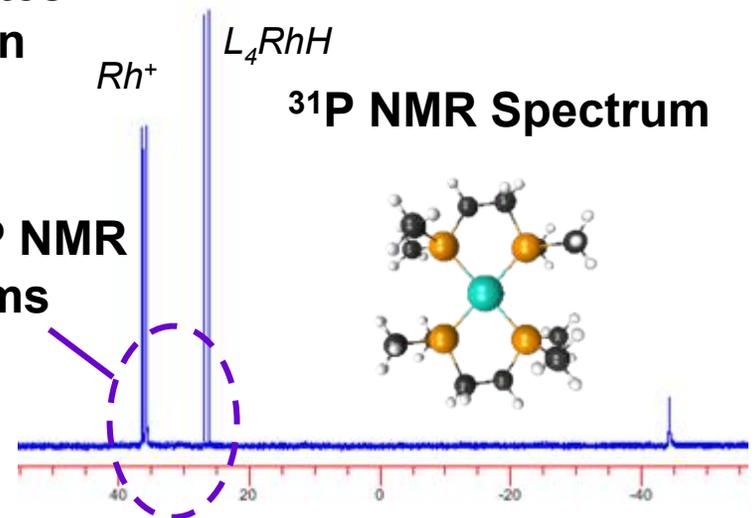
^{11}B NMR spectra at 55 °C
(1H decoupled and coupled):



Proposed for FY08

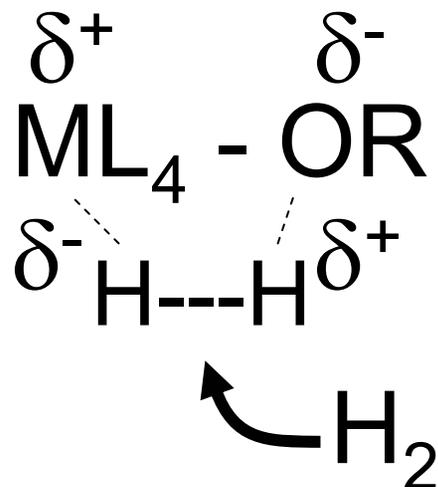


Shift in ^{31}P NMR
Confirms



PNNL: Mock, Potter, Dubois, Camaioni

Use of Theory and Experiment to Understand Energetics is Key to Efficient Regeneration



Step 1: H₂ Activation

H₂ + pressure + heat

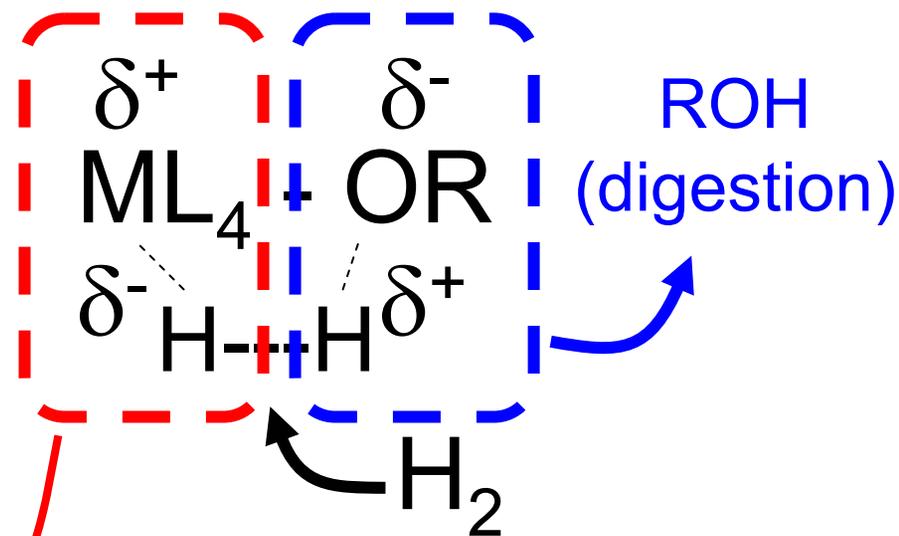
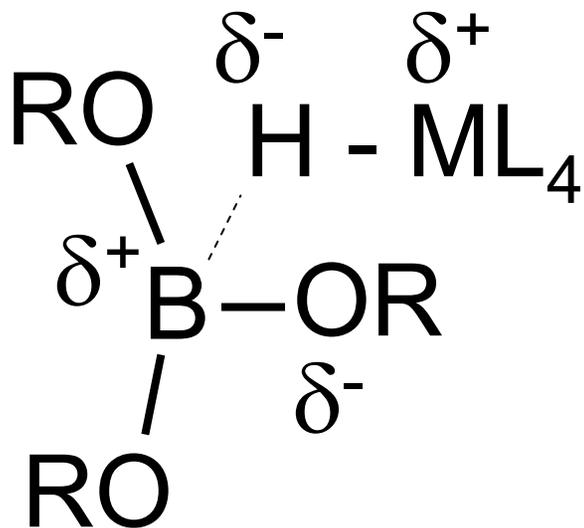
Metal: H₂ → H⁺ & H⁻ (not H•)

Understanding the Mechanism & Energetics

Key to Solving Regeneration Problem

Step 2: Reduction

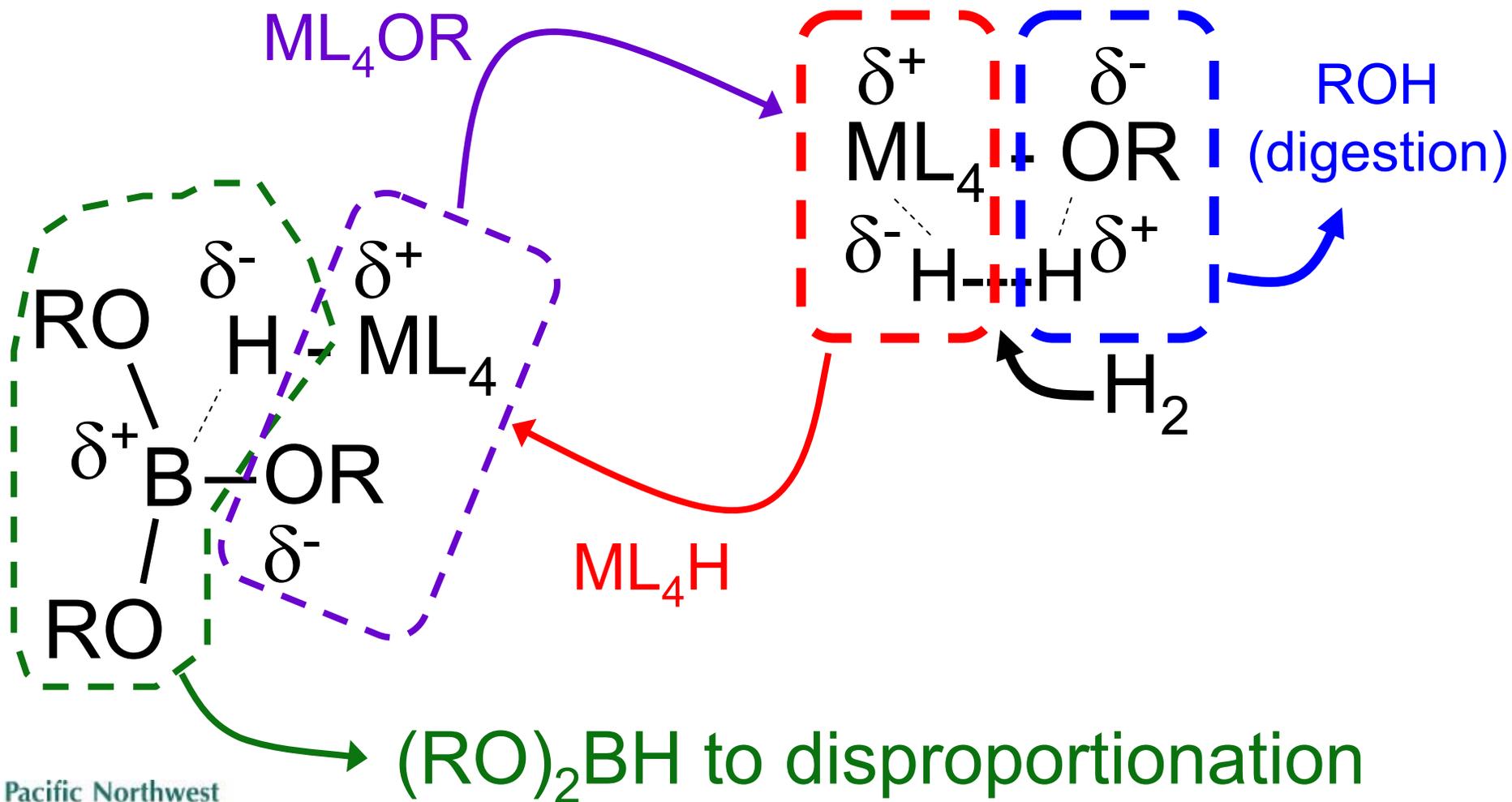
Hydricity of donor must be matched to acceptor strength



Acidity of proton donor critical:
acceptor ROH must be more
stable than ML_4OR

Understanding the Mechanism & Energetics

Key to Solving Regeneration Problem

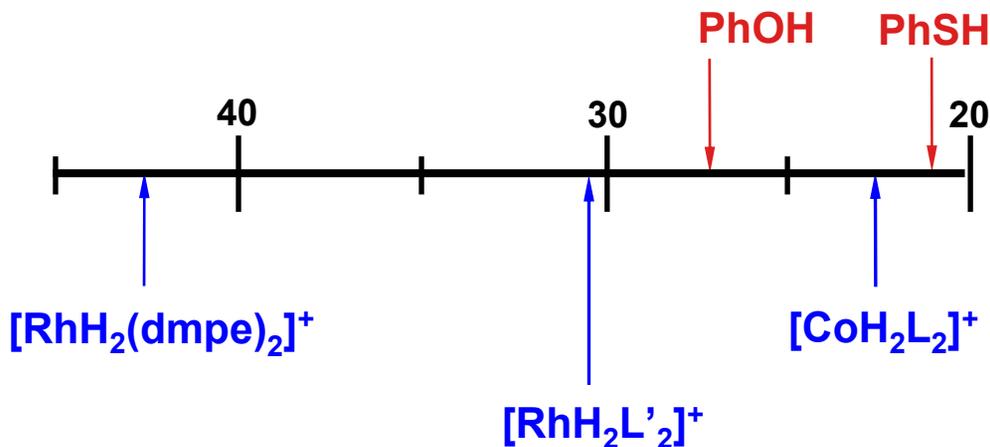
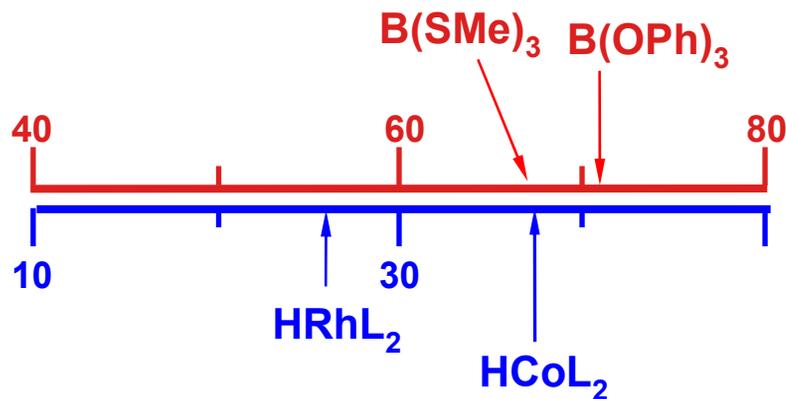


Matching Hydricity and pK_a for MH_2 and HX

M, L, & R are the tuning parameters!!

Hydride Affinity ($-\Delta H$): $BX_3 + H^- \rightarrow HBX_3^-$
(calculation)

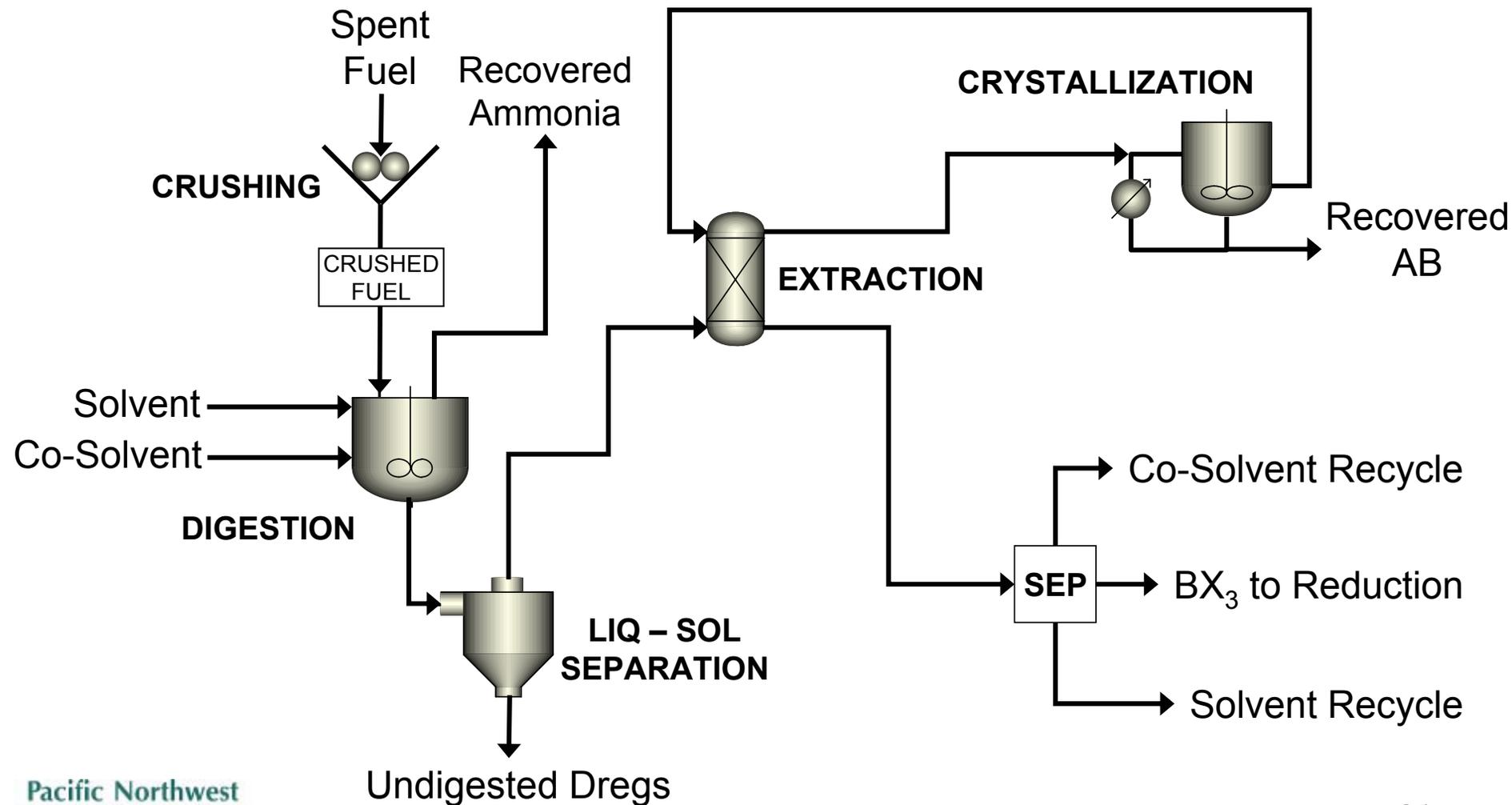
Hydride Donor Abilities (ΔG):
 $HML_2 \rightarrow ML_2^+ + H^-$ (measured)



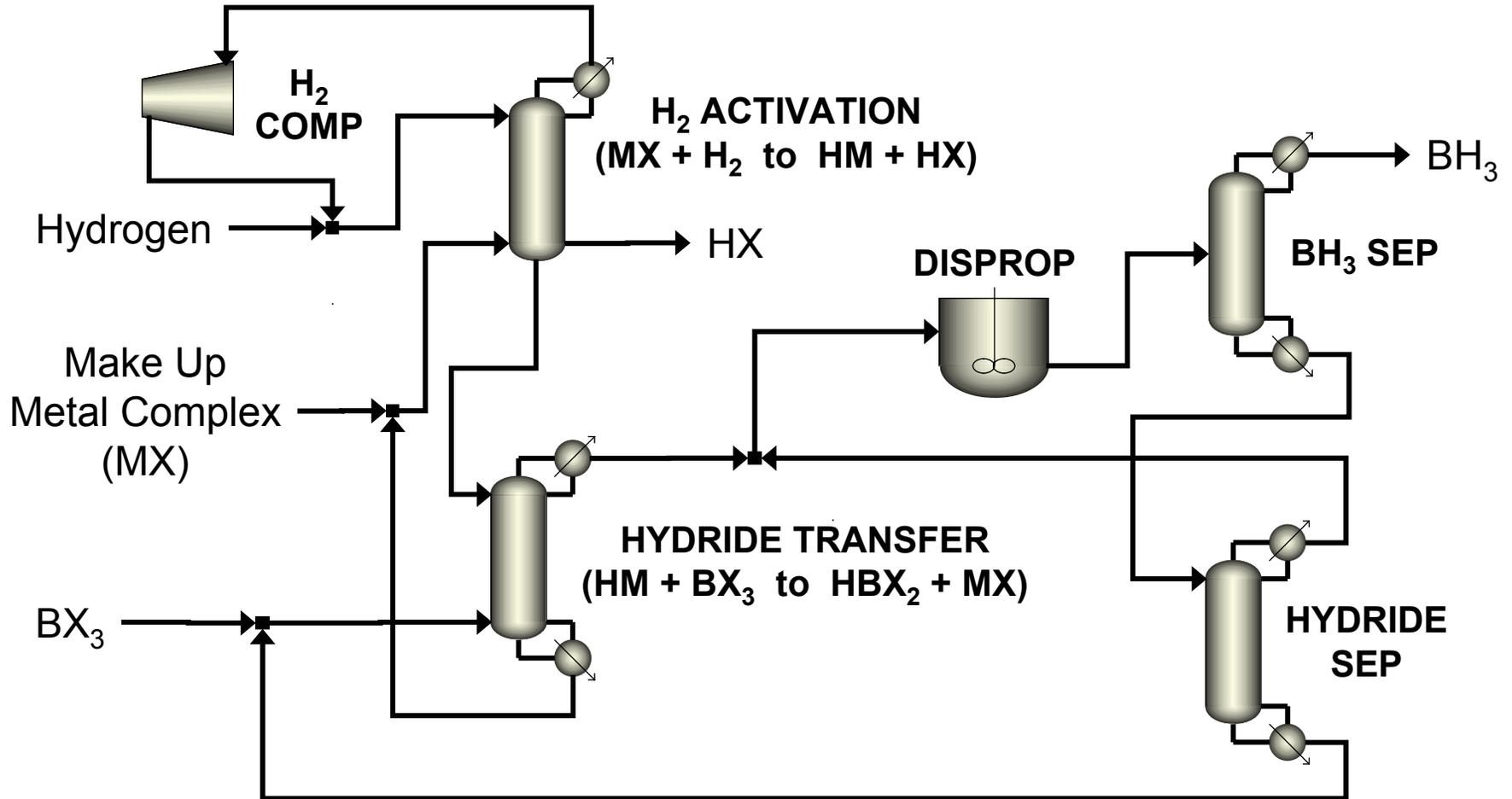
pK_a : $HX \rightleftharpoons H^+ + X^-$

pK_a : $[MH_2L_n]^{m+} \rightleftharpoons H^+ + [MHL_n]^{(m-1)+}$

Preliminary flow sheets can indicate gaps: Digestion



Reduction



Lessons Learned from Flow Sheeting: Technical Gaps to Address in Phase 2

- Although processes have been conceived: very limited optimization of operating envelopes
 - Demonstration of the chemistry in small scale, batch mode
 - Continuous processing still quite an extrapolation from here
- Spent Fuel: Residual BH Recovery
 - Do we capture H⁻ in spent fuel as hydride during digestion or as H₂ to be converted to hydride during reduction?
 - Assessment of energy penalty vs. process complexity still in progress
- Hydride Separation
 - Critical separation step: BX₃-BHX₂
 - Need data on thermal stability, relative volatility, solubility, etc.
- Mixed Solvents
 - Digestion and reduction processes may require different solvents
 - Separations: Is solubility the only consideration?
- Ammonia Borane Heat Sensitivity
 - Difficult to separate AB from other hydrides based on volatility
- Physical Properties of Organo-boranes
 - Needed for process design
- Additional focus on the separations will be required moving ahead

Summary

- Release
 - Kinetics can be increased dramatically through hybrid materials (LiAB)
 - Method for foam suppression in AB discovered
 - Can now pursue solids handling in earnest
 - Enables system volumetric density much higher than previously possible
 - Initial results indicate ABH_2 worth further study
- Regeneration
 - Experiments confirm theory for reduction of $B(OPh)_3$ w/MH
 - Digestion well in hand; reduction pathway becoming clearer
 - Preliminary regeneration flow sheets have helped identify needed separations work
- Milestones on track & Phase 2 now underway

Future Work

- Release – focus now on materials down-selected by the Center
 - Additional focus on materials within the metal-AB family: LiAB is interesting; others?
 - ABH_2 : exactly how stable can it be?
 - B-N-C materials
 - Characteristics of monolithic solid AB
- Regeneration
 - Push toward matching energetics of reduction with digestion agent choice
 - Synthetic challenges in the Co system
 - Quantification of yields and process envelopes
 - Work toward filling gaps in process knowledge (with ROH, LANL, Penn, UC Davis) and understand efficiency/cost
 - Help LANL, Penn by matching PNNL reduction strategy with their digestion chemistries

Team & Collaborators

PNNL supports collaboration through expertise in materials science, instrumentation, theory & simulation, inorganic chemistry, high field NMR, general characterization of hydrogen bearing materials, and engineering support for on-board and off-board

Center of Excellence
for Chemical
Hydrogen Storage



PNNL Team

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