DOE Hydrogen Program

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

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

Project ST5

Overview

Timeline

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

Barriers Addressed

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

Budget

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

Center Collaborations

Los Alamos NATIONAL LABORATORY EST. 1943

Penn University of Pennsylvania

The University of Alabama

Rohm and Haas

UC Davis University of California

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BORAX

University of Washington

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

PNNL

- 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

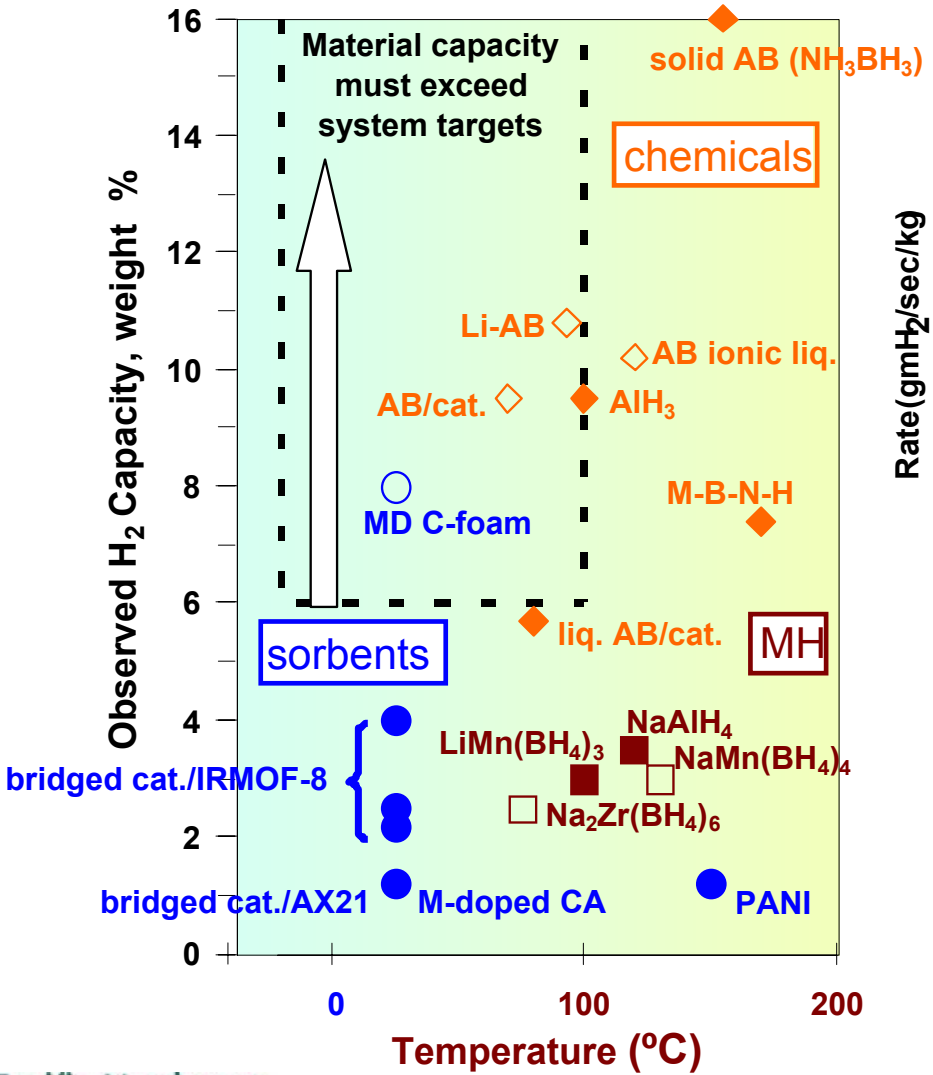
Major Achievements for the Review Period

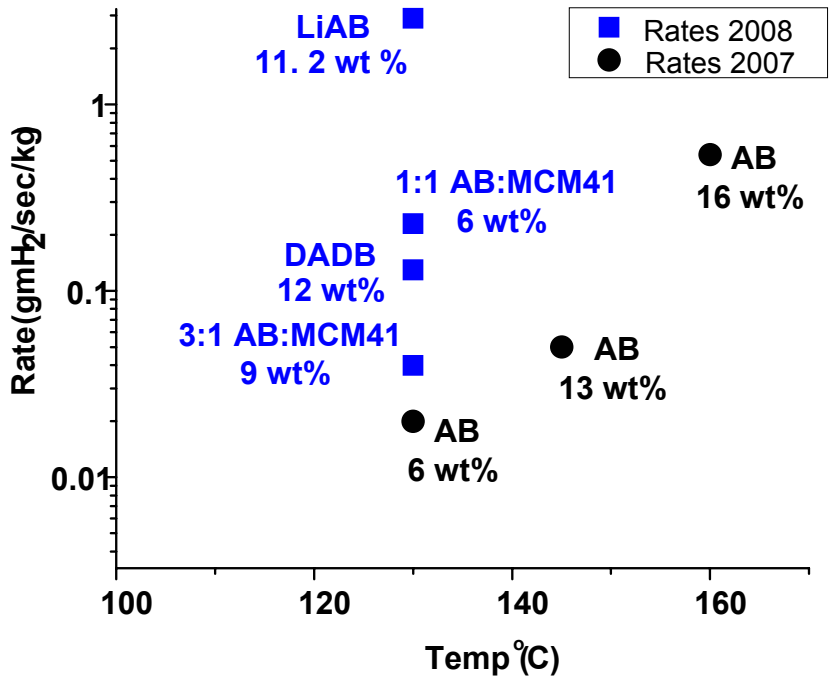
- Developed Li-NH_2-BH_3 under IPHE collaboration: worth additional pursuit: H_2 release kinetics increased by order of magnitude
- Discovered additives that suppress foaming of NH_3BH_3: enables pursuit of engineered system
- Demonstrated hydride transfer chemistry from 'activated' H_2 to spent fuel: 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
- ABH_2 kinetics too fast to measure with existing methods

PNNL: Karkamkar, Choi, Daschbach, Autrey

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Modified from Thomas & Sandrock, DOE

Summary Table

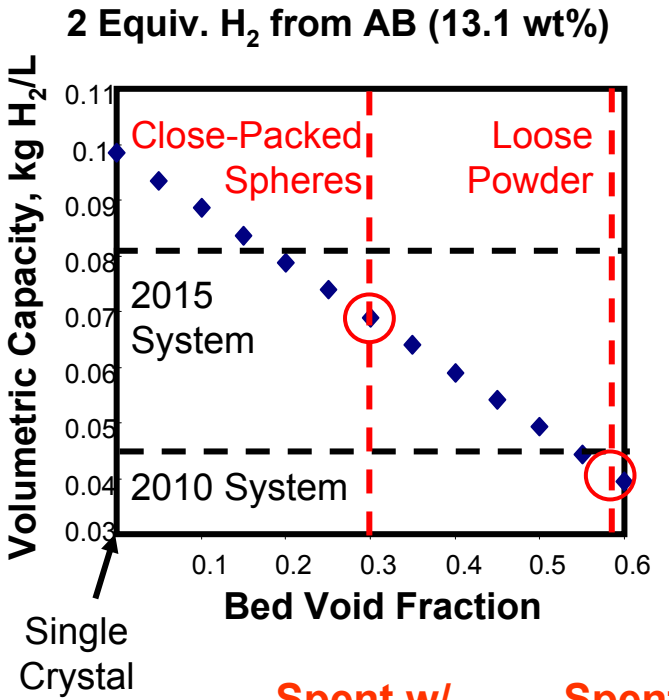
2007 – Neat AB (per kg on rates)

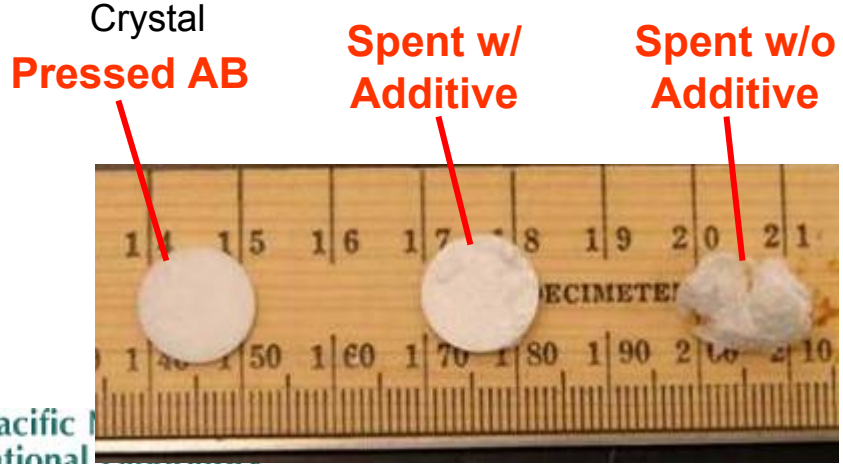
	1 eq H_2	1.5 eq H_2	2 eq H_2	2.5 eq H_2	Peak rate
160°C	50 sec (1.3 g/s)	80 sec (1.2 g/s)	240 sec (.54 g/s)	1000 sec (.16 g/s)	3.8 g/s
145°C	70 sec (.93 g/s)	200 sec (.5 g.s)	1200 sec (.11 g/s)		2.1 g/s
130°C	150sec (.43 g/s)	1000sec (.1 g/s)			1.1 g/s

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

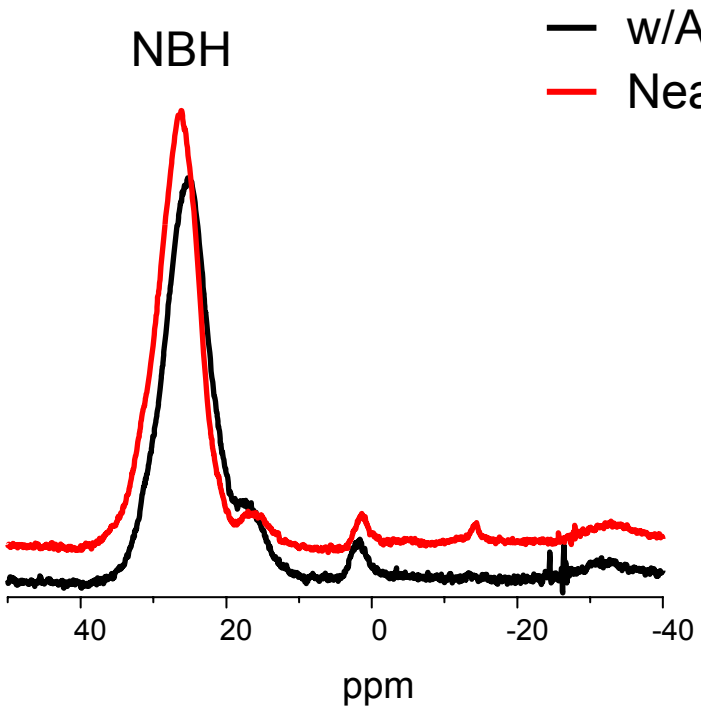




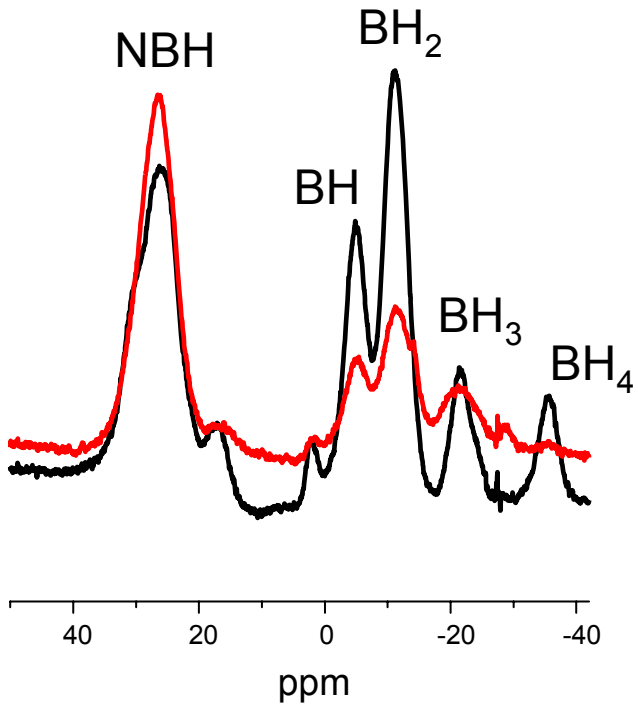
- System targets are difficult for granulated materials
- Addition of a spent fuel tank cuts the volumetric density in half
  - AB foams when it releases hydrogen – not conducive to engineering
  - Potential show stopper
- Campaign on anti-foaming initiated in Q1, FY08
  - More than 50 additive formulations 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

PNNL: Choi, Karkamkar, Aardahl, Autrey

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



155°C: 2 – 2.2 Eq. H_2

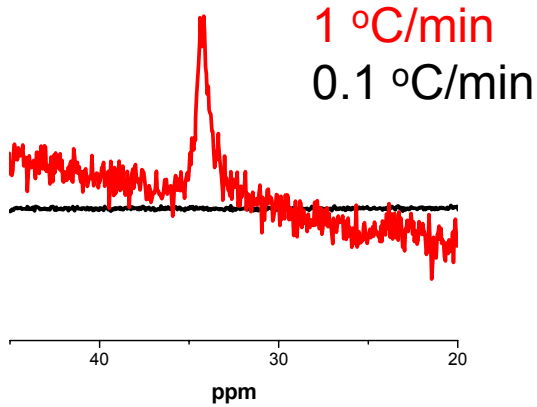


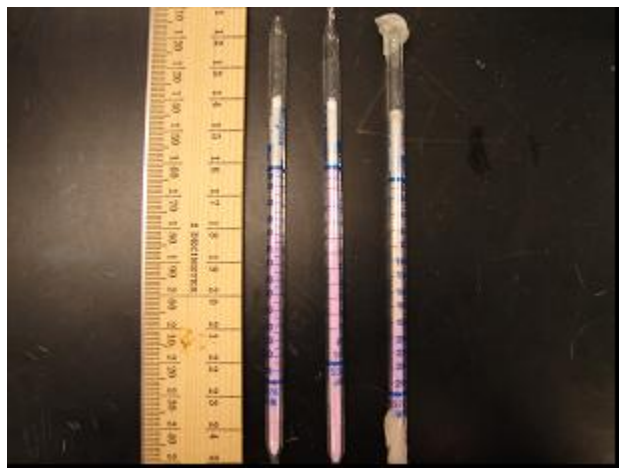
120°C: 1.3 Eq. H_2

PNNL: Choi, Karkamkar, Autrey

Measurements of Volatile Impurities Show Small Amounts of Borazine and NH_3

- Pass H_2 though THF to trap borazine → measure via NMR
  - 1 °C/min (detected)
  - 0.1 °C/min (not detected)
- Daigger tube (Kitagawa)
  - Measure [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

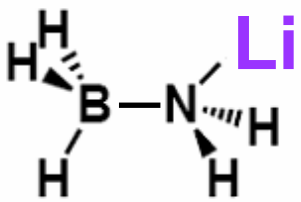




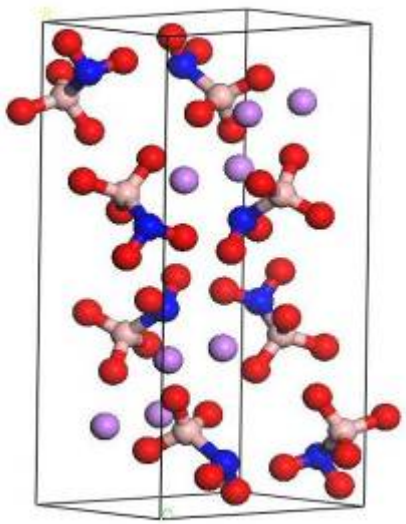
PNNL: Karkamkar, Autrey

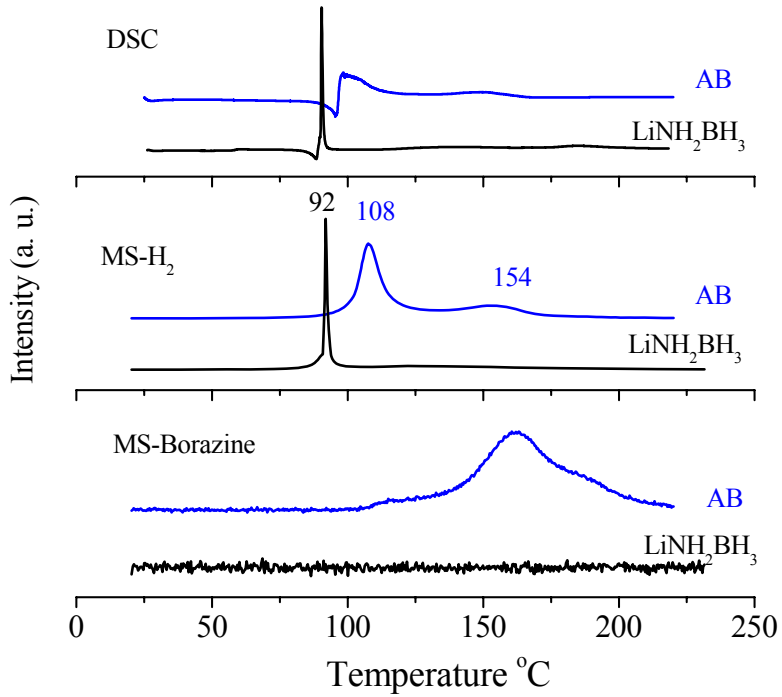
Li-AB: Fast Kinetics & Little Barrier on Second Equivalent of H_2 (all release < 100°C)

- 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.

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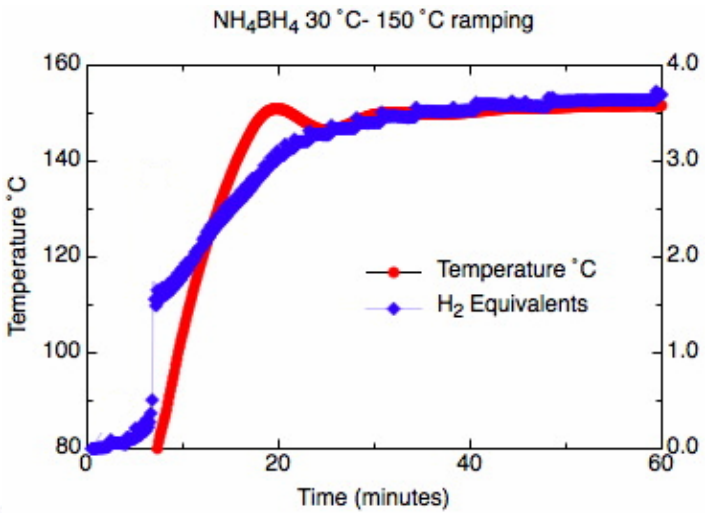
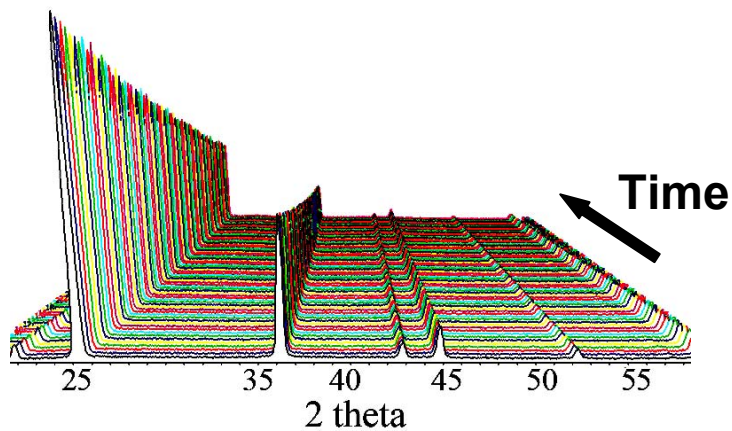
IPHE

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: $ABH_2 \rightarrow AB + H_2$
- Step 2: $ABH_2 + AB \rightarrow DADB \rightarrow PAB + H_2$
- Complete reaction (150°C): 20 wt% H_2





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

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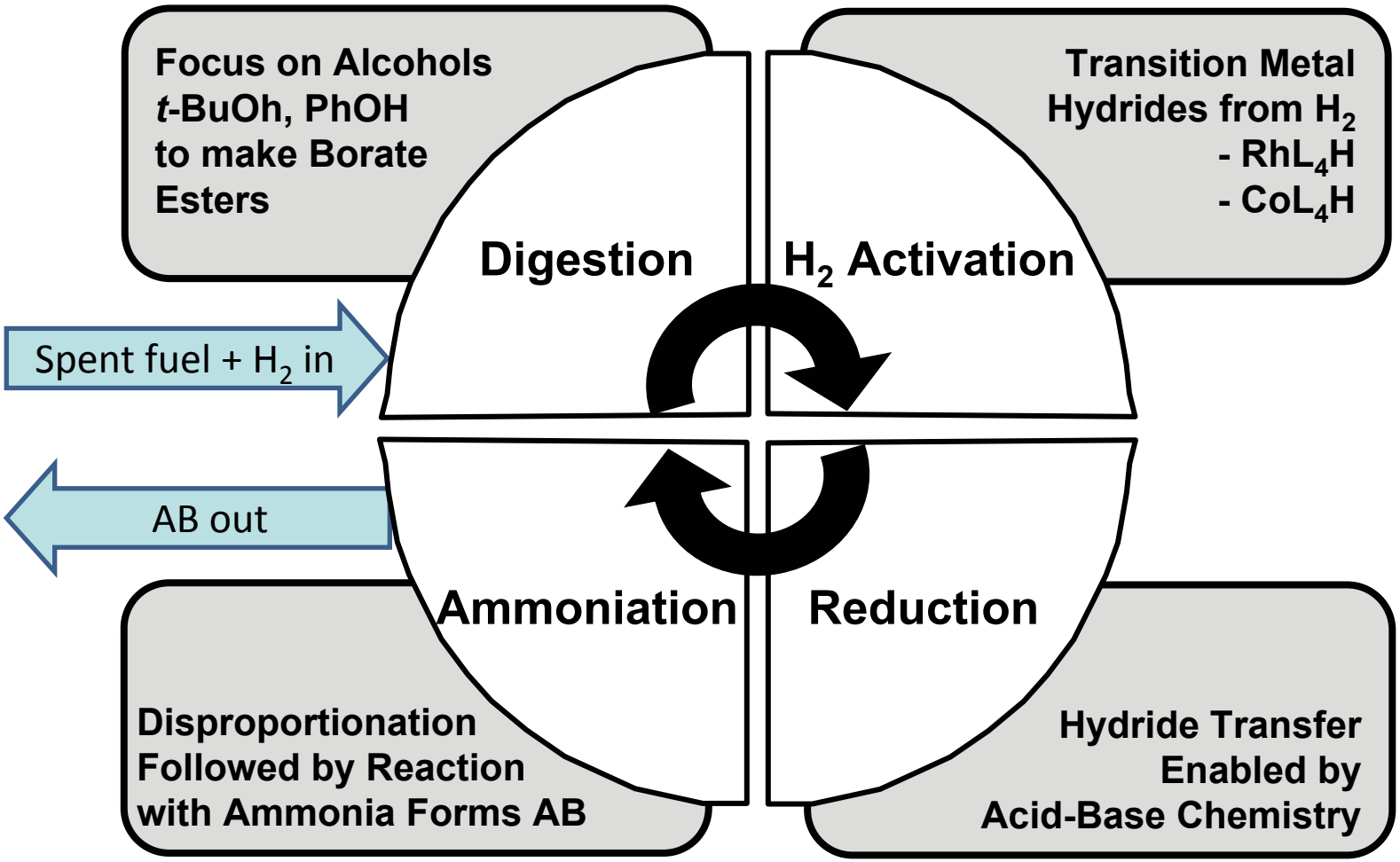
PNNL: Karkamkar, Heldebrant, Autrey

Proposed at 2007 AMR: Regeneration of AB with 'Activated' H_2



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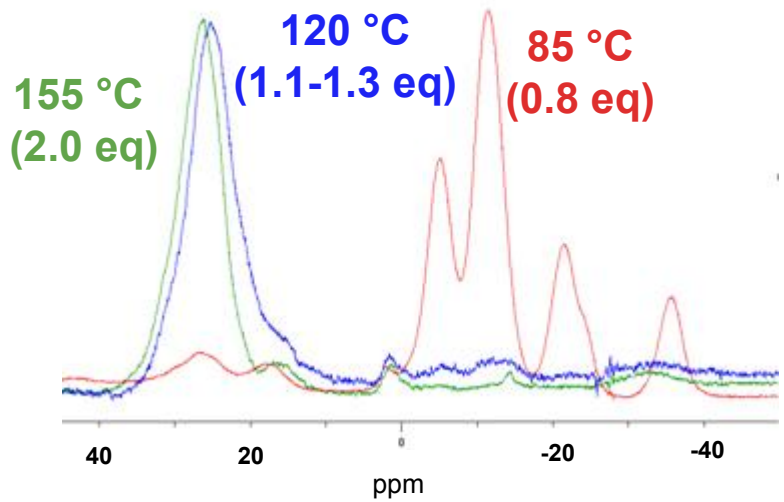
PNNL: Camaioni, Dubois, Mock, Potter, Heldebrant, Rassat, Zheng

NMR Characterization Key to Confirming Efficient Regeneration Chemistry

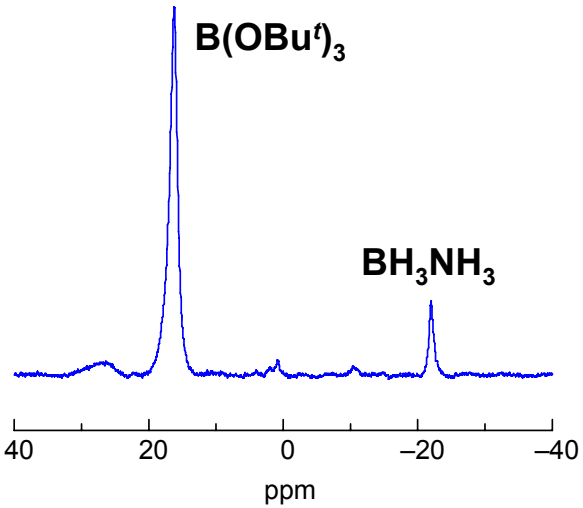
Solid ^{11}B: 800 MHz



***t*-BuOH**

NH_3

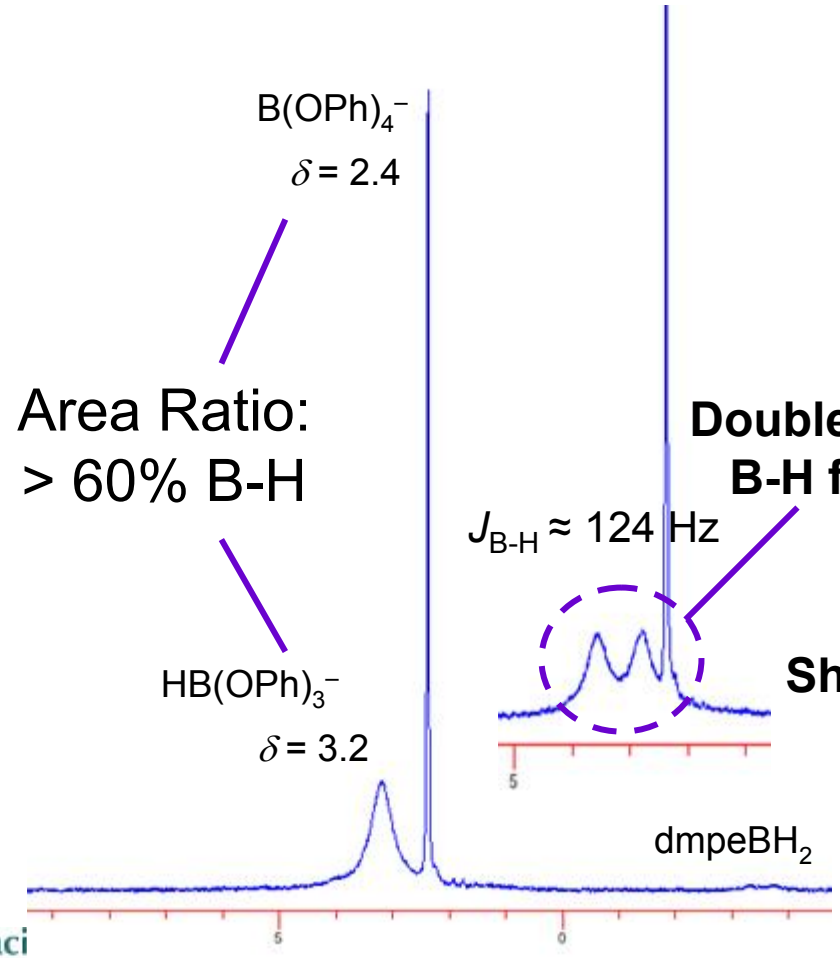
Solution ^{11}B: 300 MHz



- ≥ 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):

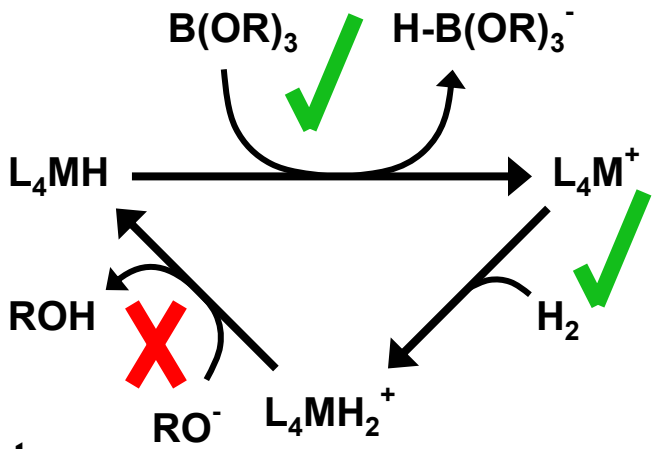


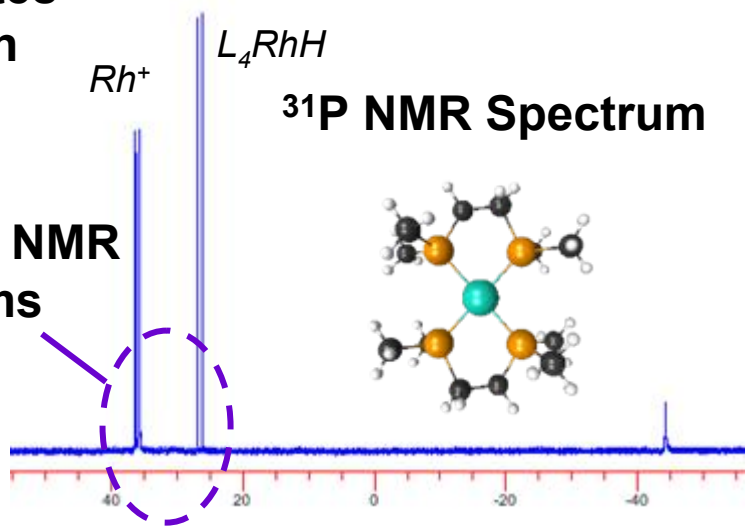
Area Ratio:
> 60% B-H

Doublet indicates B-H formation

Shift in ^{31}P NMR Confirms

Proposed for FY08

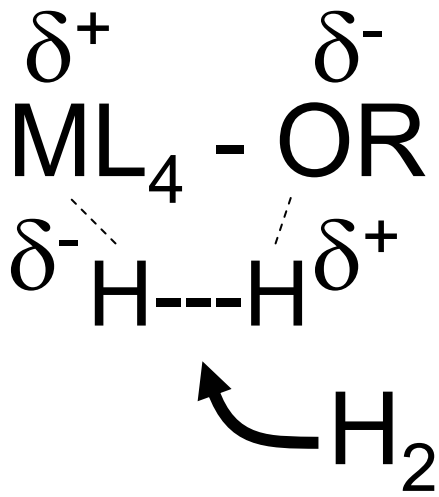




^{31}P NMR Spectrum

PNNL: Mock, Potter, Dubois, Camaioni

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



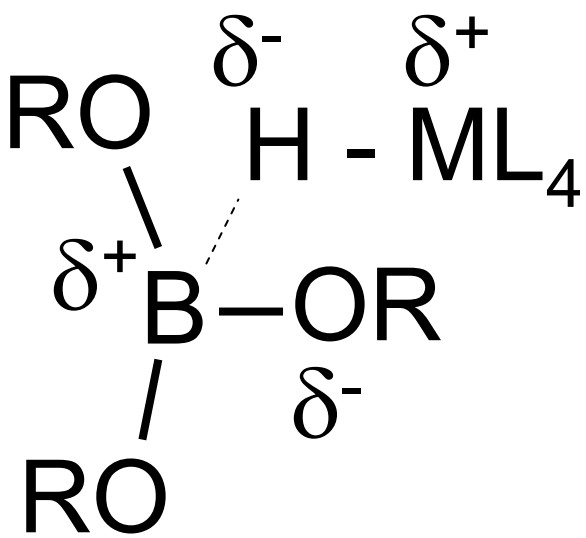
Step 1: H_2 Activation

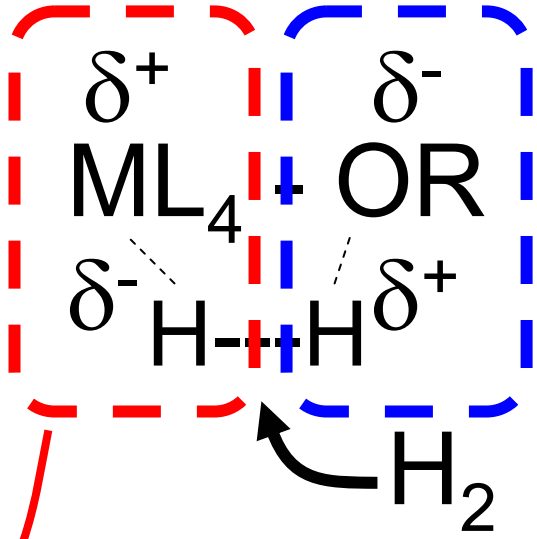
H_2 + pressure + heat

Metal: $H_2 \rightarrow H^+$ & H^- (not H•)

Understanding the Mechanism & Energetics Key to Solving Regeneration Problem

Step 2: Reduction
Hydricity of donor must be matched to acceptor strength



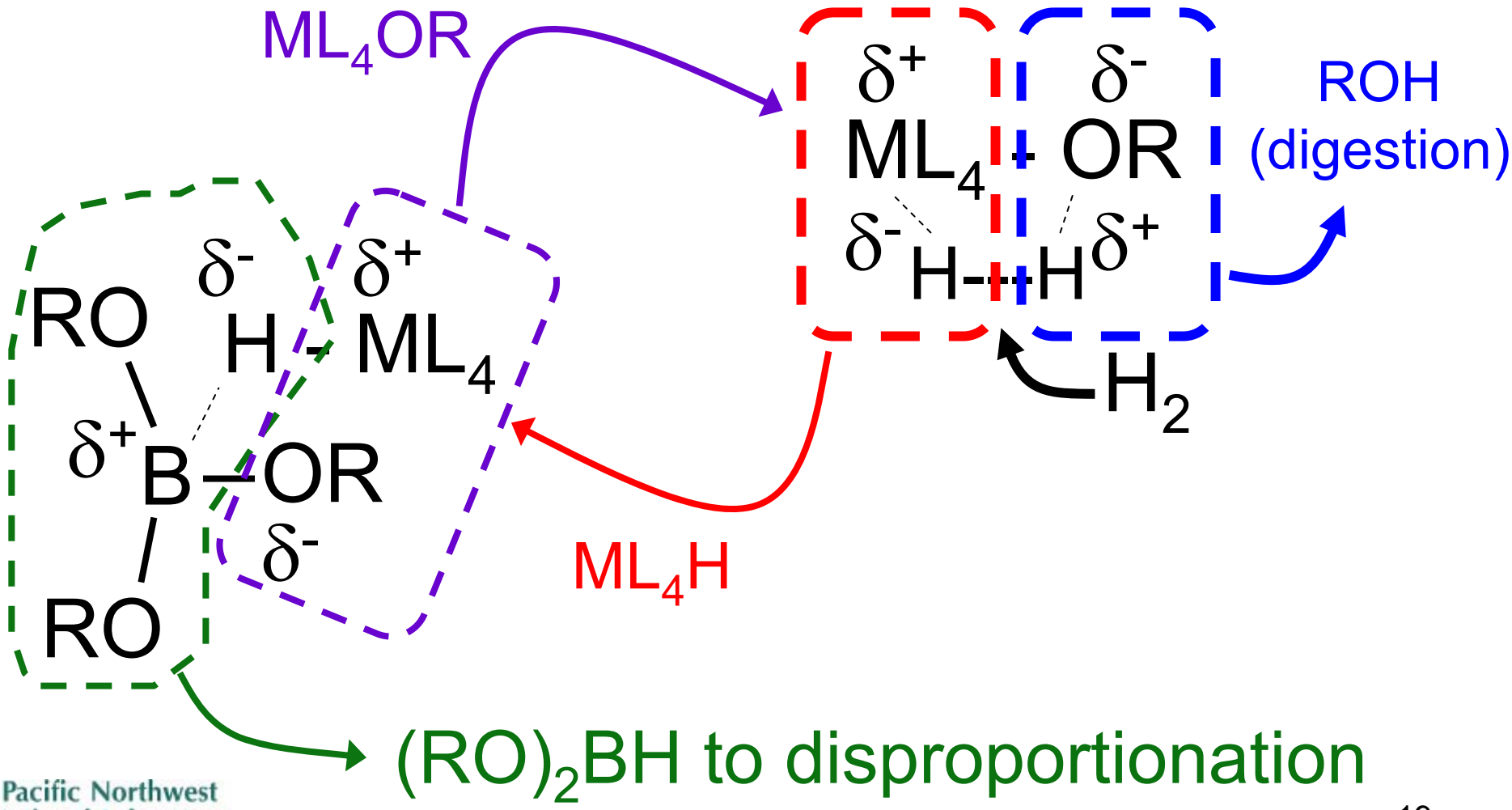


ROH (digestion)

ML_4H

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

Understanding the Mechanism & Energetics Key to Solving Regeneration Problem



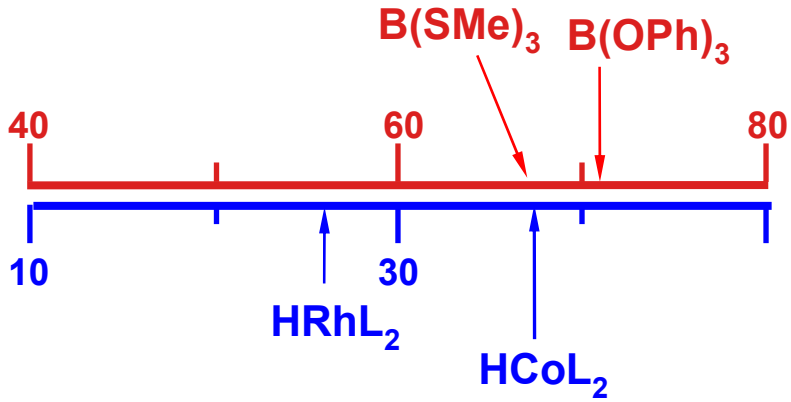
Matching Hydricity and pK_a for MH_2 and HX
M, L, & R are the tuning parameters!!

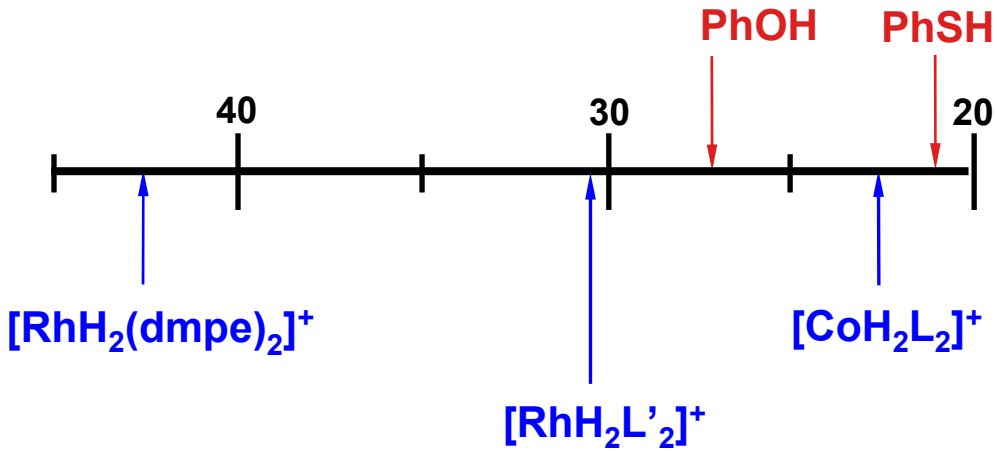
Hydride Affinity (-ΔH): $BX_3 + H^- \rightarrow HBX_3^-$

(calculation)

Hydride Donor Abilities (ΔG):

$HML_2 \rightarrow ML_2^+ + H^-$ (measured)

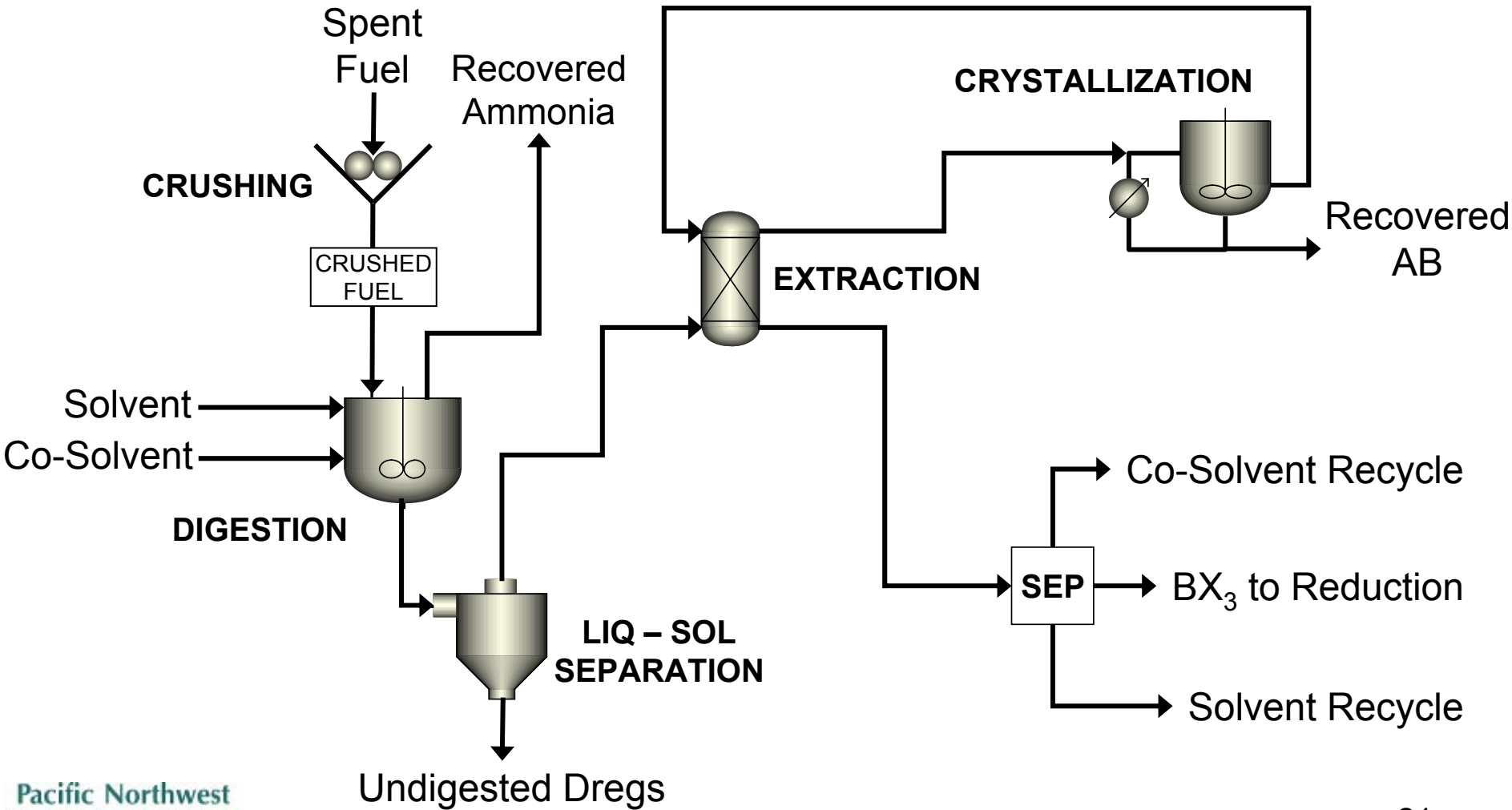




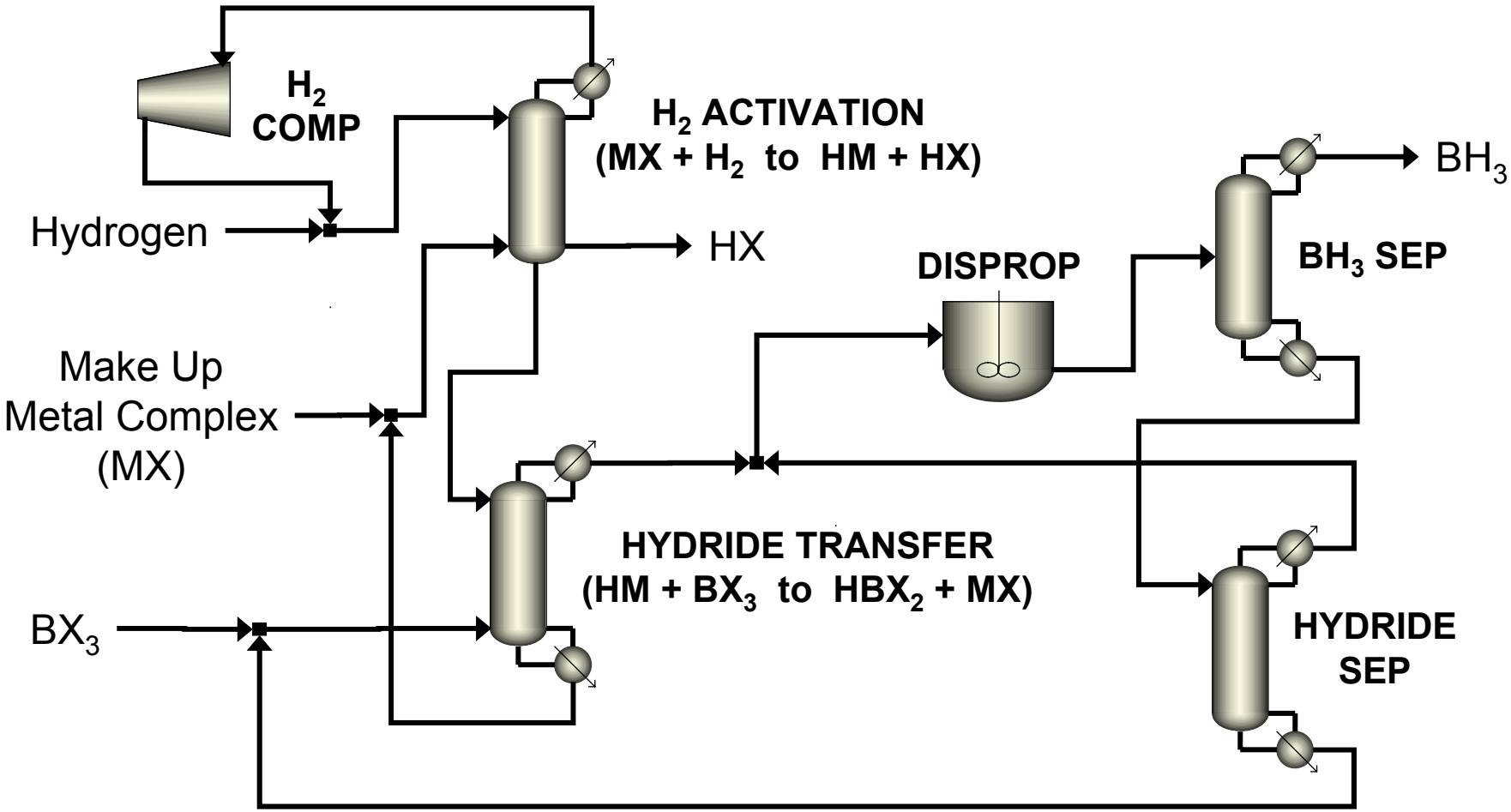
pK_a: $HX \leftrightarrows H^+ + X^-$

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

Preliminary flow sheets can indicate gaps: Digestion



Reduction


H_2 COMP
H_2 ACTIVATION ($MX + H_2$ to $HM + HX$)
Hydrogen
HX
DISPROP
BH_3
BH_3 SEP
Make Up Metal Complex (MX)
HYDRIDE TRANSFER ($HM + BX_3$ to $HBX_2 + MX$)
BX_3
HYDRIDE SEP

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 H_2 to be converted to hydride during reduction?
  - Assessment of energy penalty vs. process complexity still in progress
- Hydride Separation
  - Critical separation step: BX_3-BHX_2
  - 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

International Partnership for the Hydrogen Economy

Pacific Northwest National Laboratory
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H_2 RELEASE

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