DOE Hydrogen Program

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

Chris Aardahl, PNNL

June 2008

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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

Project STP3

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: $1600K
  - $100K Equipment
- 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

Borax

University of Washington

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

Project Objectives & Approach

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 (amine boranes and their derivatives)
  - NH_3BH_3 (& isomers), NH_4BH_4, related compounds
  - Hybrid materials of B-N compounds and metal-hydrides
  - Develop process chemistry for the regeneration of NH_3BH_3
- Support Center partners through expertise and instrumentation for theory & simulation, high field NMR, general characterization of hydrogen bearing materials, and engineering support for on-board and off-board

Objectives 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
- 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

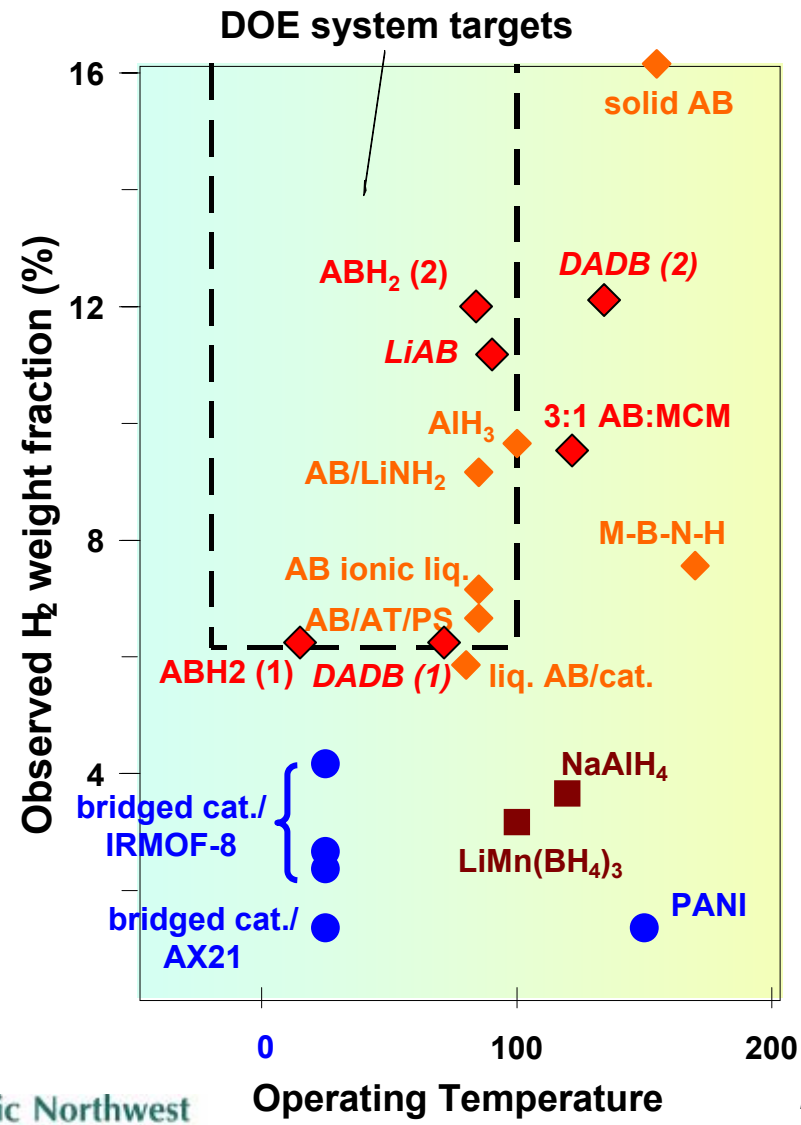
Major Achievements for the Review Period

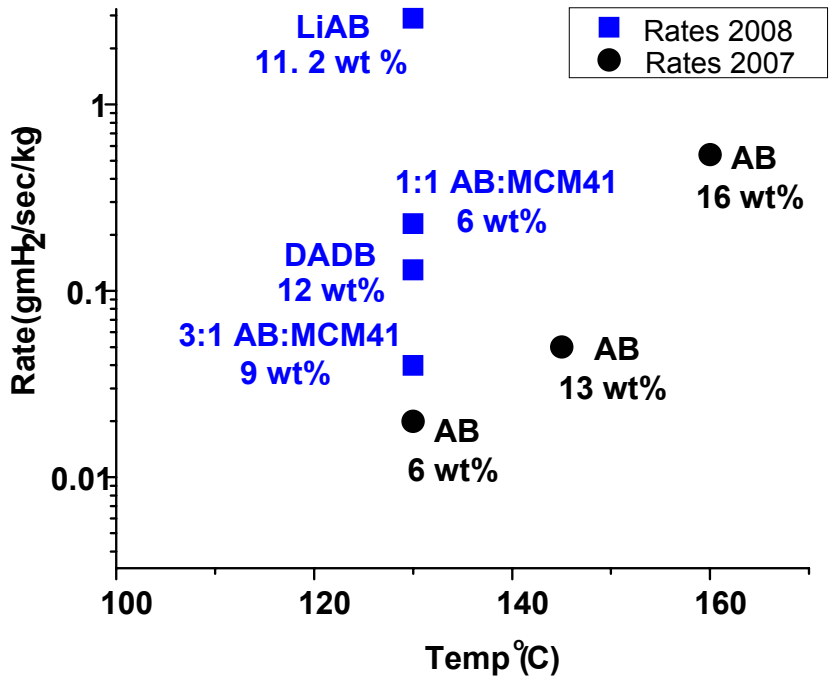
- Developed Li-NH_2-BH_3 under IPHE collaboration: worth additional pursuit: fast kinetics with good capacity
- Discovered additives that suppress foaming of NH_3BH_3: enables pursuit of engineered system
- Demonstrated hydride transfer chemistry from 'activated' H_2 to spent fuel: new 'catalytic' route for fuel regeneration has promise for efficiency targets
- Preliminary flow sheets for regeneration developed and being used to pin point gaps in process knowledge
- Characterized the impurities from NH_3BH_3 and $LiNH_2BH_3$ systems

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)



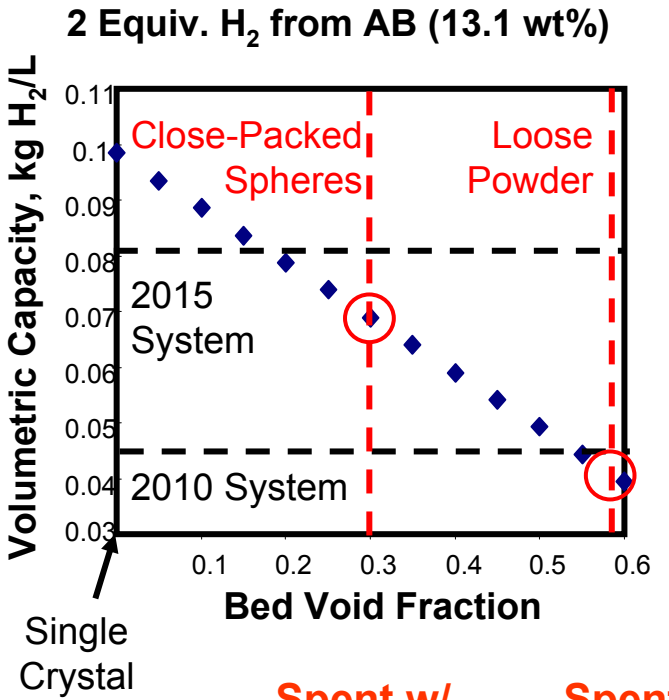


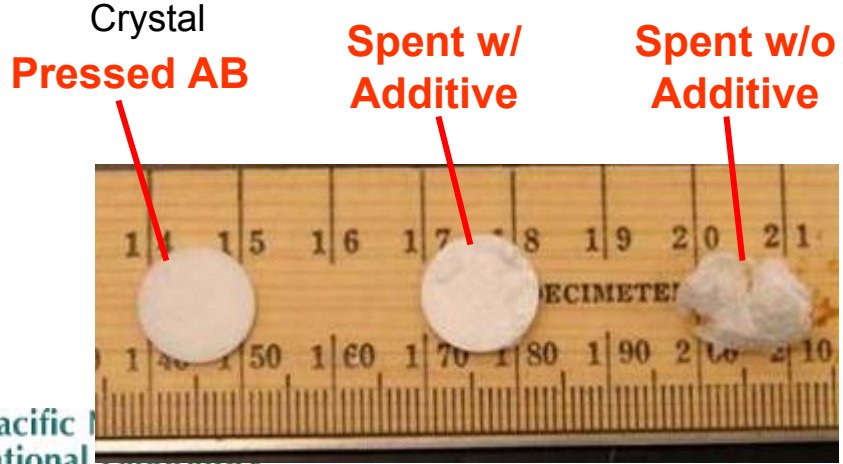
- Order of magnitude increase in release rates
- ABH_2 kinetics too fast to measure with existing methods

PNNL: Karkamkar, Choi, Daschbach, Autrey

Modified from G. Thomas *et al.*, DOE (April 2007)

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

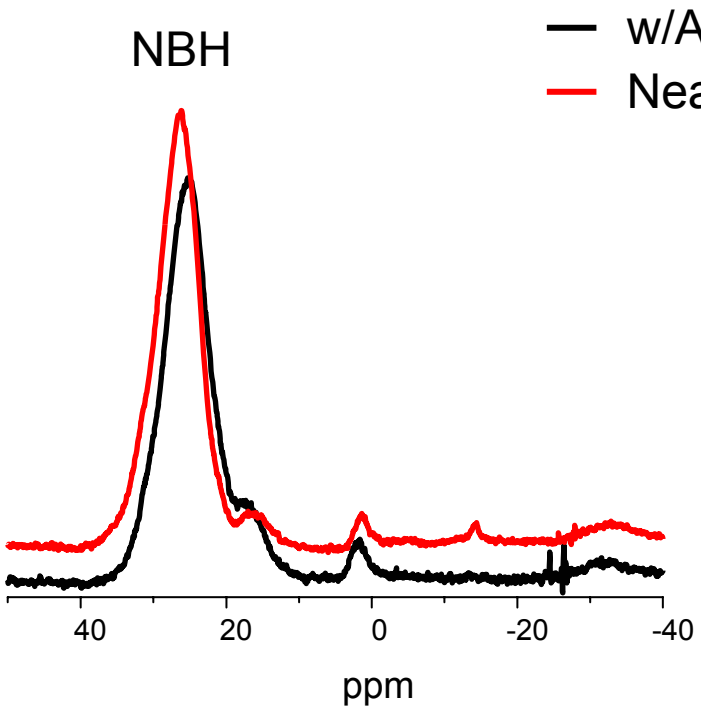




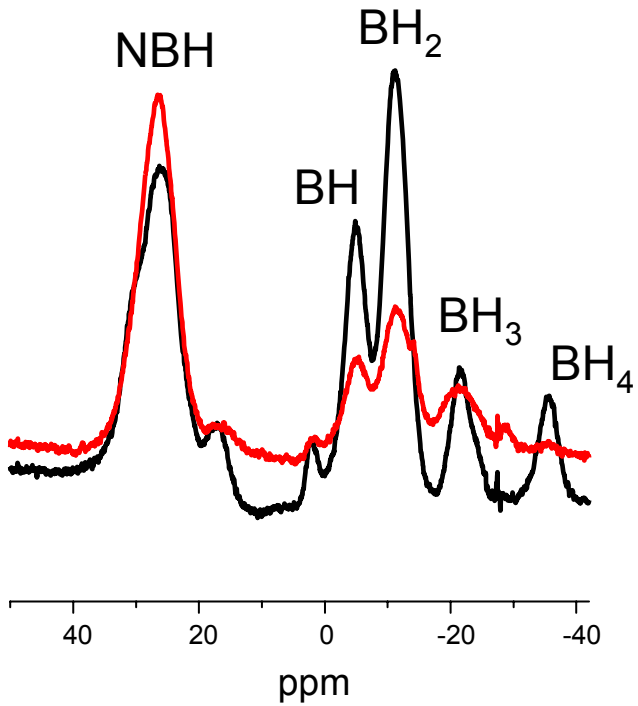
- System targets are difficult for granulated materials
- Addition of a spent fuel tank cuts the volumetric density in half
  - AB foams when it releases hydrogen – not conducive to engineering
  - Potential show stopper
- Campaign on anti-foaming initiated in Q1, FY08
  - More than 50 additive formulations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

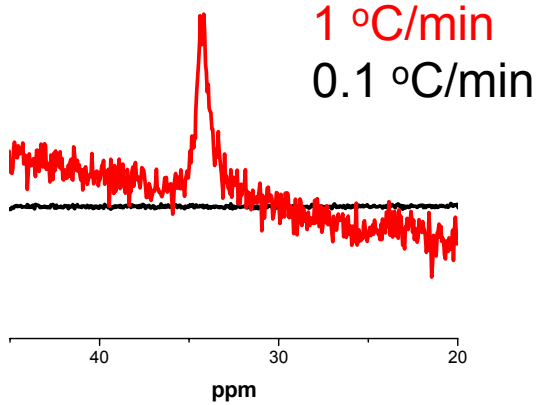


120°C: 1.3 Eq. H_2

PNNL: Choi, Karkamkar, Autrey

Measurements of Volatile Impurities Show Small Amounts of Borazine and NH_3

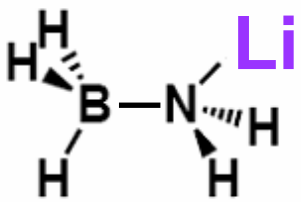
- Pass H_2 though THF to trap borazine → measure via NMR
  - 1 °C/min (detected)
  - 0.1 °C/min (not detected)
- Daigger tube (Kitagawa)
  - Measure [NH_3] in H_2 from gas burette
  - Isothermal (120 °C; 1.3 eq H_2): NH_3 ca. 170 ±10 ppm
  - Unclear whether a decomposition product or residual from synthesis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



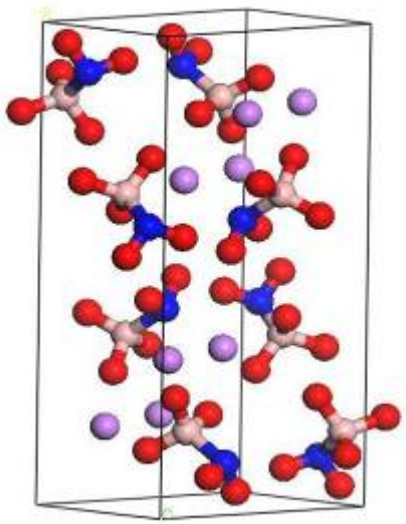
PNNL: Karkamkar, Autrey

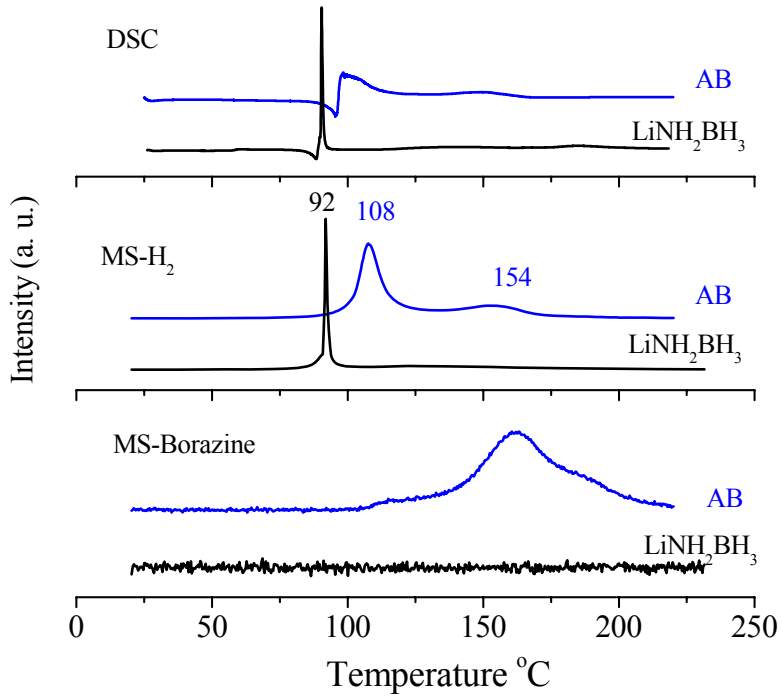
Li-AB: Fast Kinetics & Little Barrier on Second Equivalent of H_2 (all release < 100°C)

- 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

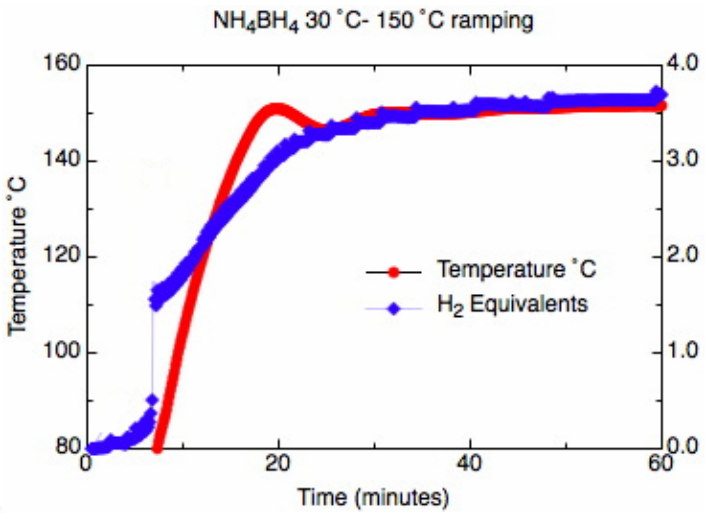
Xiong *et al.* (2008) *Nature Materials* 7, 138.

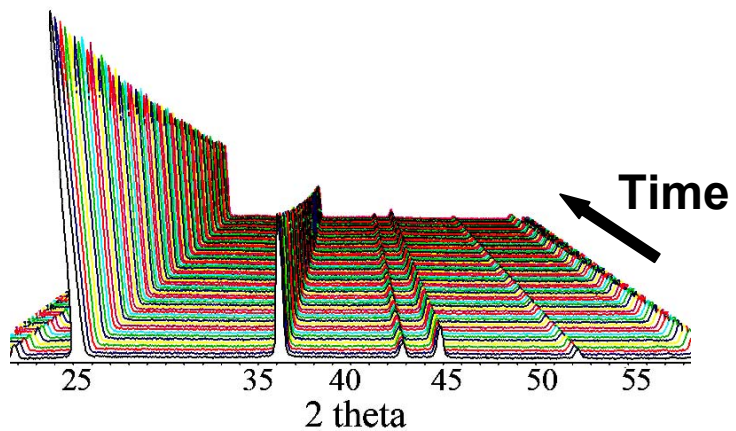
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

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



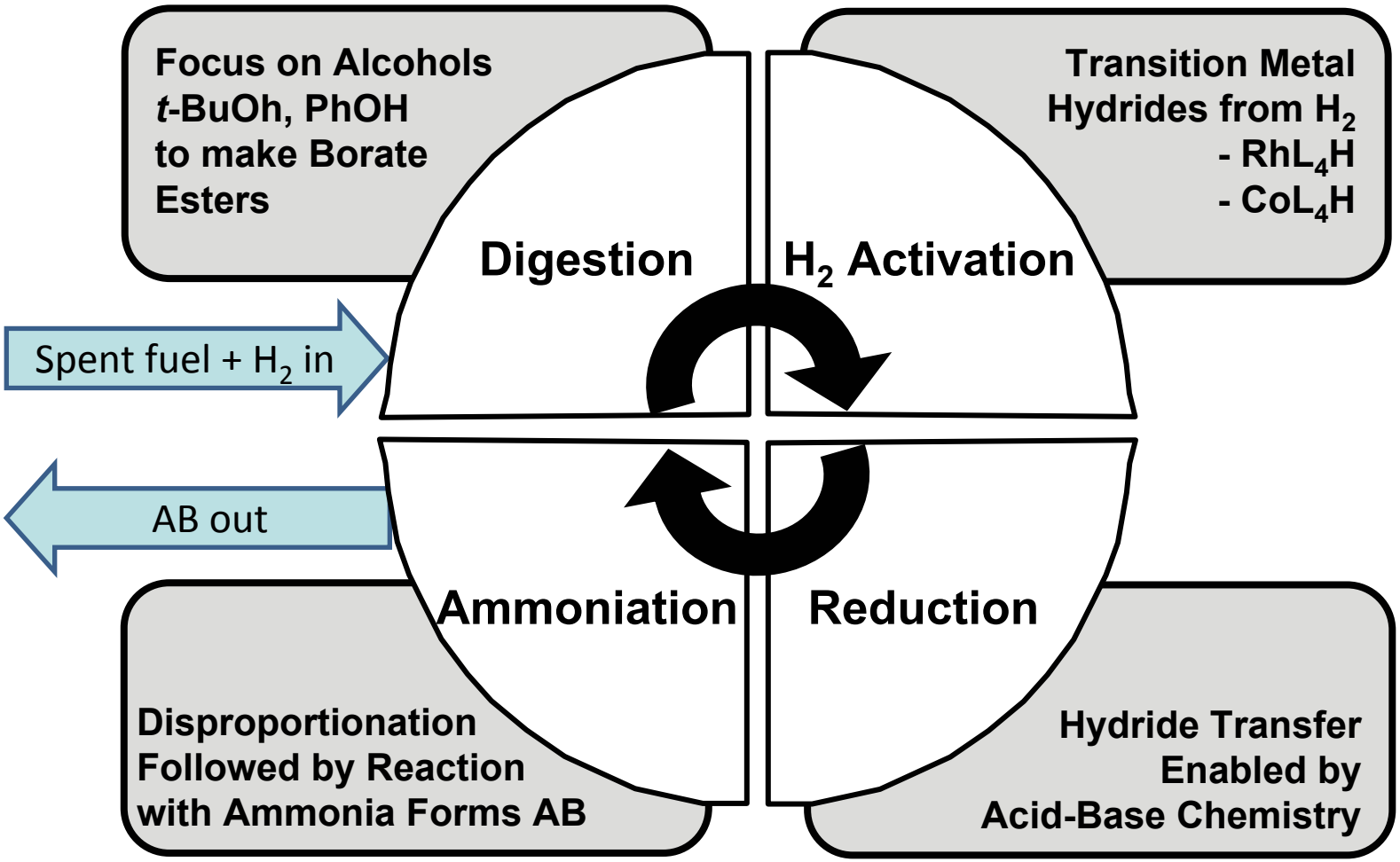


XRD of ABH_2: $t_{1/2}$= 16hrs under ambient

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

PNNL: Karkamkar, Heldebrant, Autrey

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

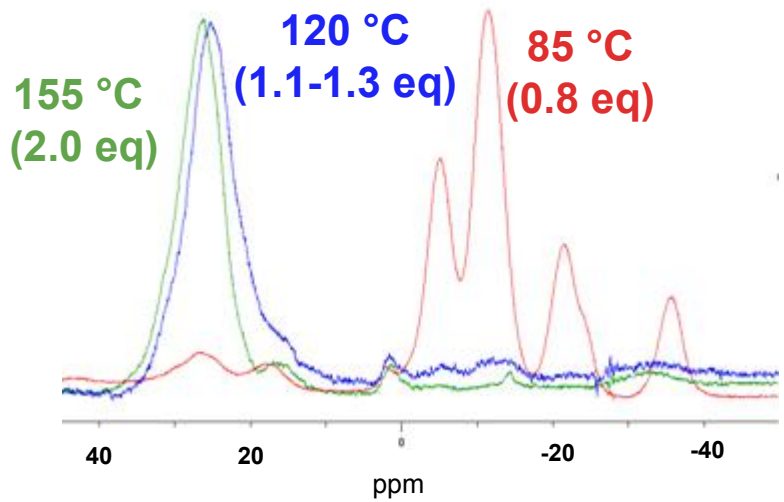


Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

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

NMR Characterization Key to Understanding Regeneration Chemistry

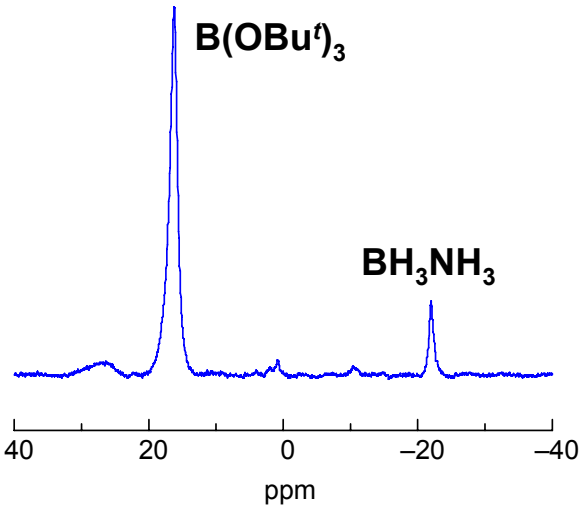
Solid ^{11}B: 800 MHz



t-BuOH

NH_3

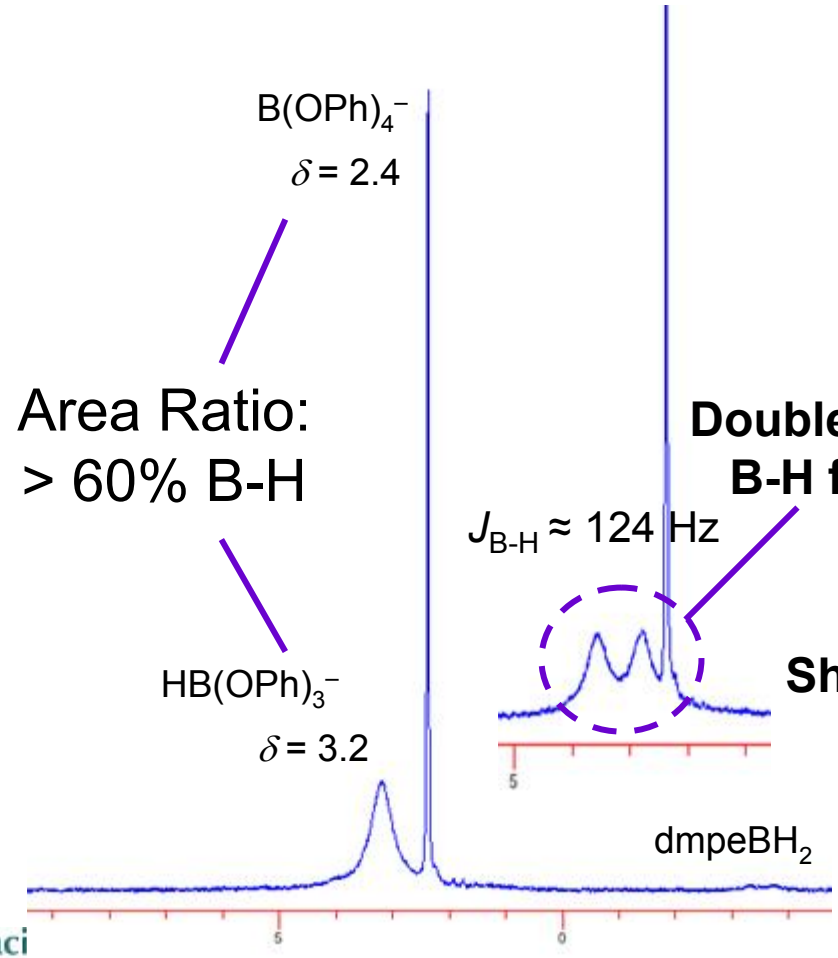
Solution ^{11}B: 300 MHz



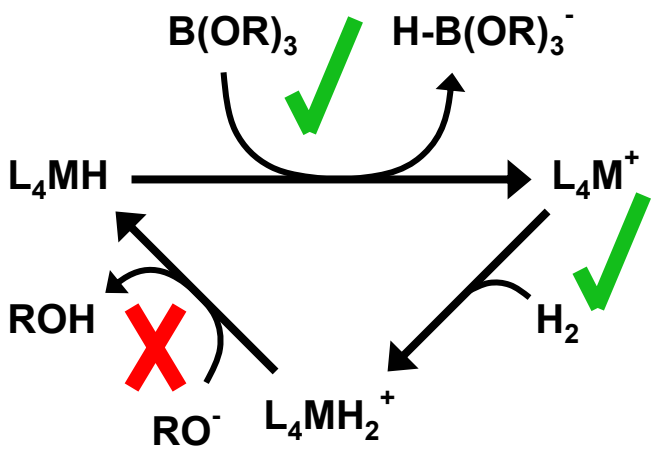
- ≥ 2 eq H_2 gives polyborazylene-like products
- Polyborazylene undergoes digestion relatively easily
- Spent fuel characterization complete
- Digestion pathways in good shape
- Principle focus in FY08 on reduction chemistry

NMR confirms $(dmpe)_2RhH$ can reduce $B(OPh)_3$!

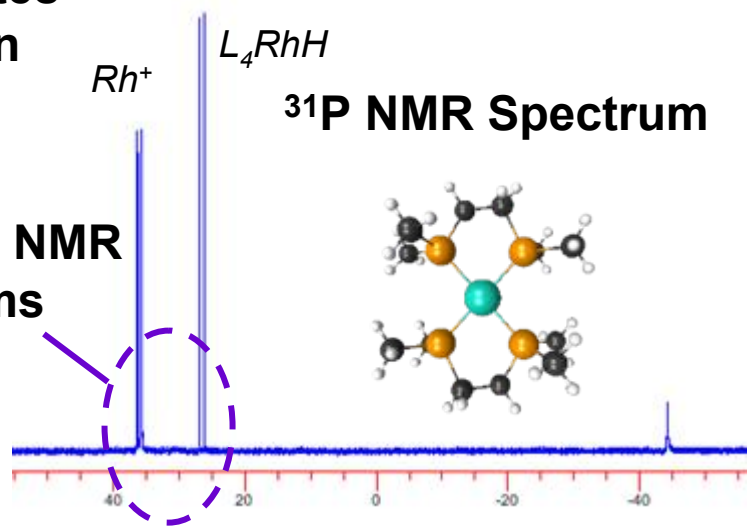
^{11}B NMR spectra at 55 °C (^1H decoupled and coupled):



Proposed for FY08



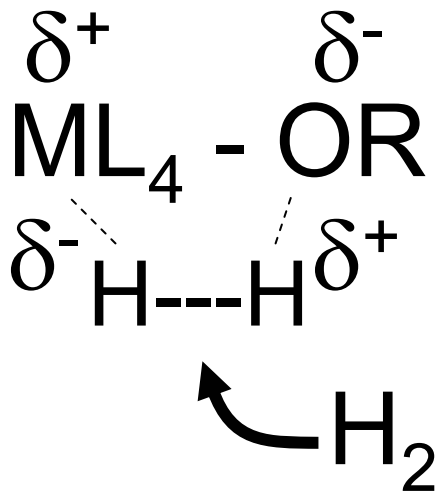
Shift in ^{31}P NMR Confirms



^{31}P NMR Spectrum

PNNL: Mock, Potter, Dubois, Camaioni

Understanding the Mechanism & Energetics Key to Solving Regeneration Problem



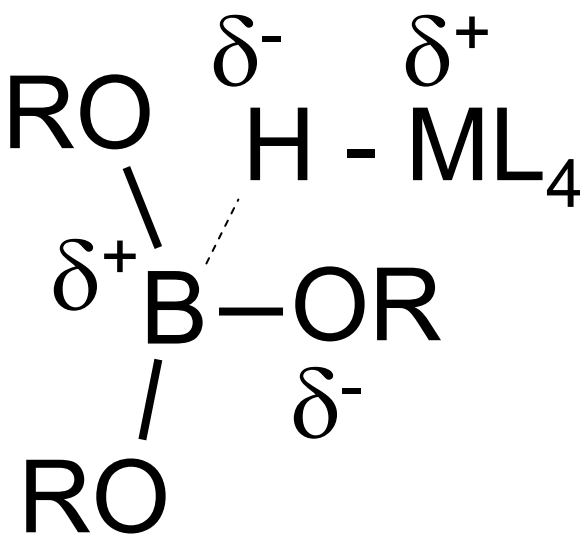
Step 1: H_2 Activation

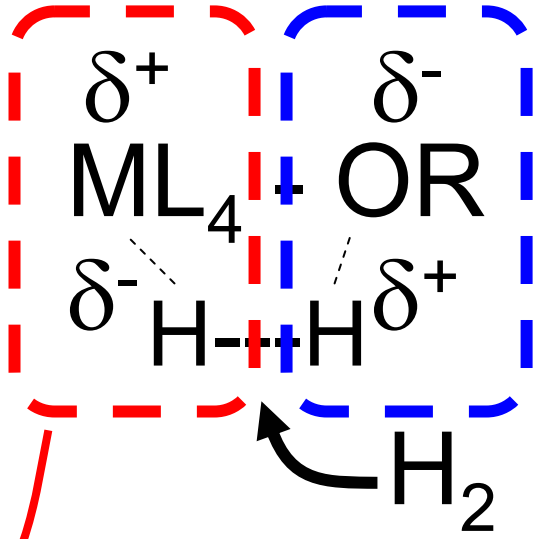
H_2 + pressure + heat

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



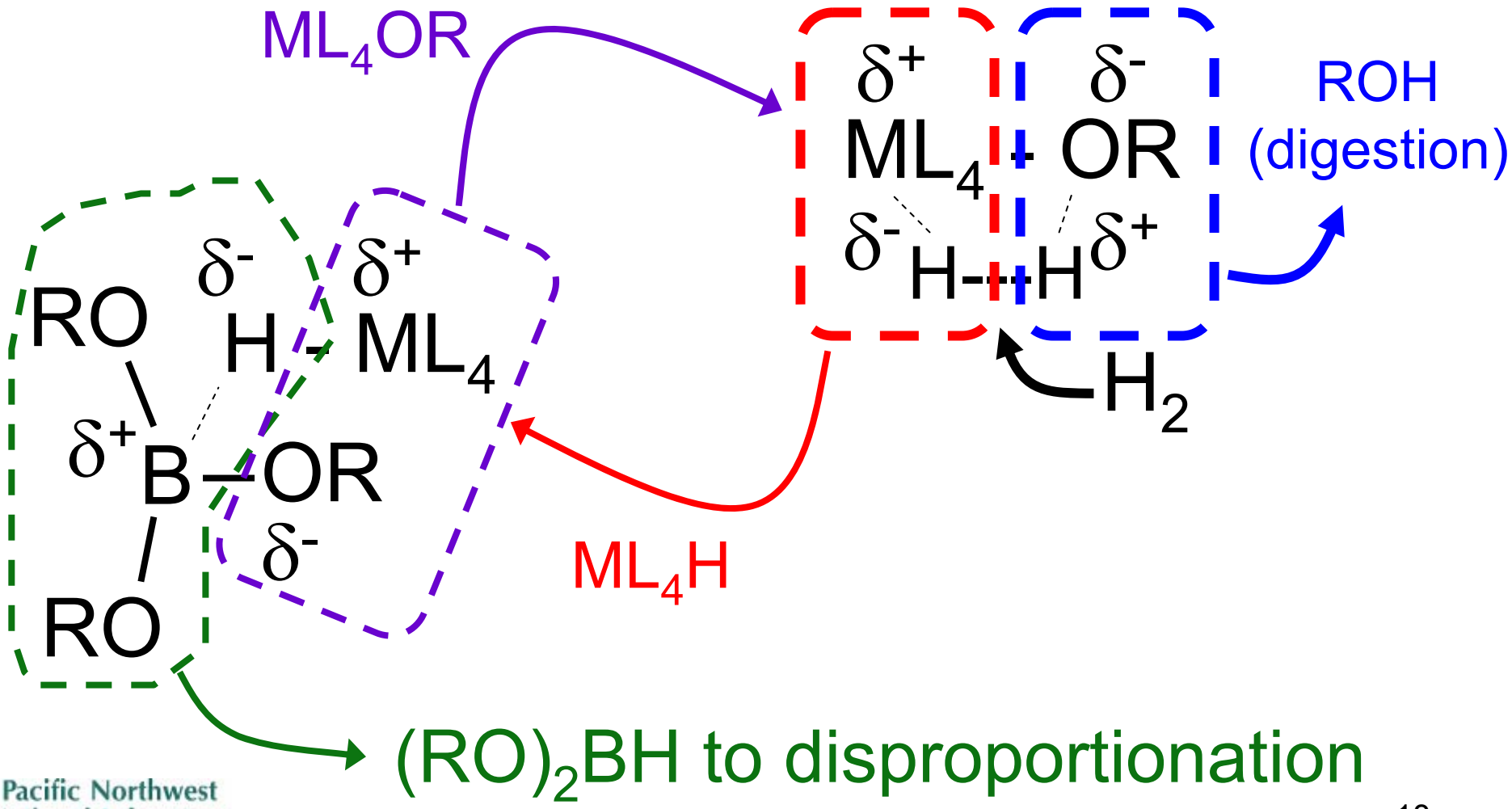


ROH (digestion)

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



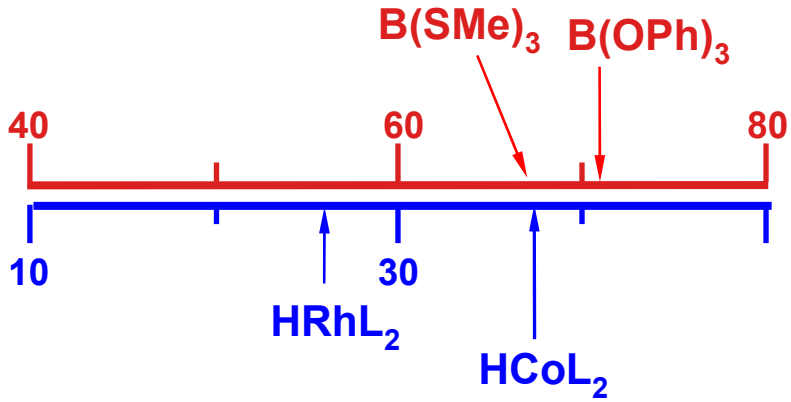
Matching Hydricity and pK_a for MH_2 and HX
M, L, & R are the tuning parameters!!

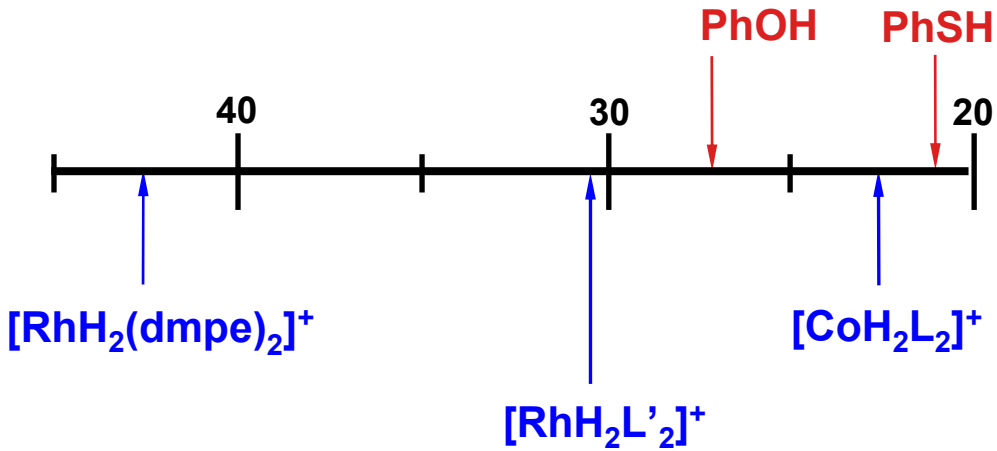
Hydride Affinity (-ΔH): $BX_3 + H^- \rightarrow HBX_3^-$

(calculation)

Hydride Donor Abilities (ΔG):

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

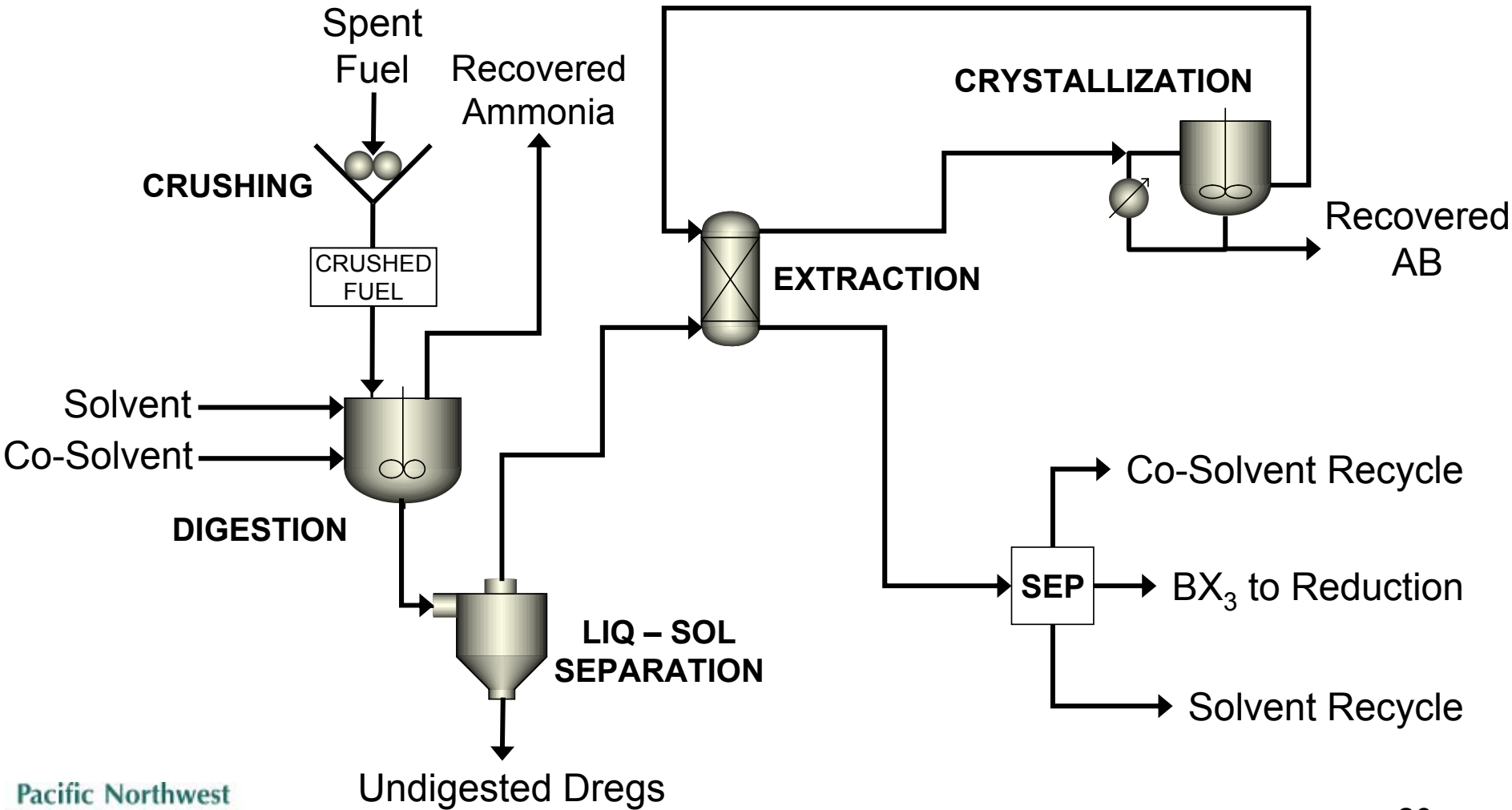




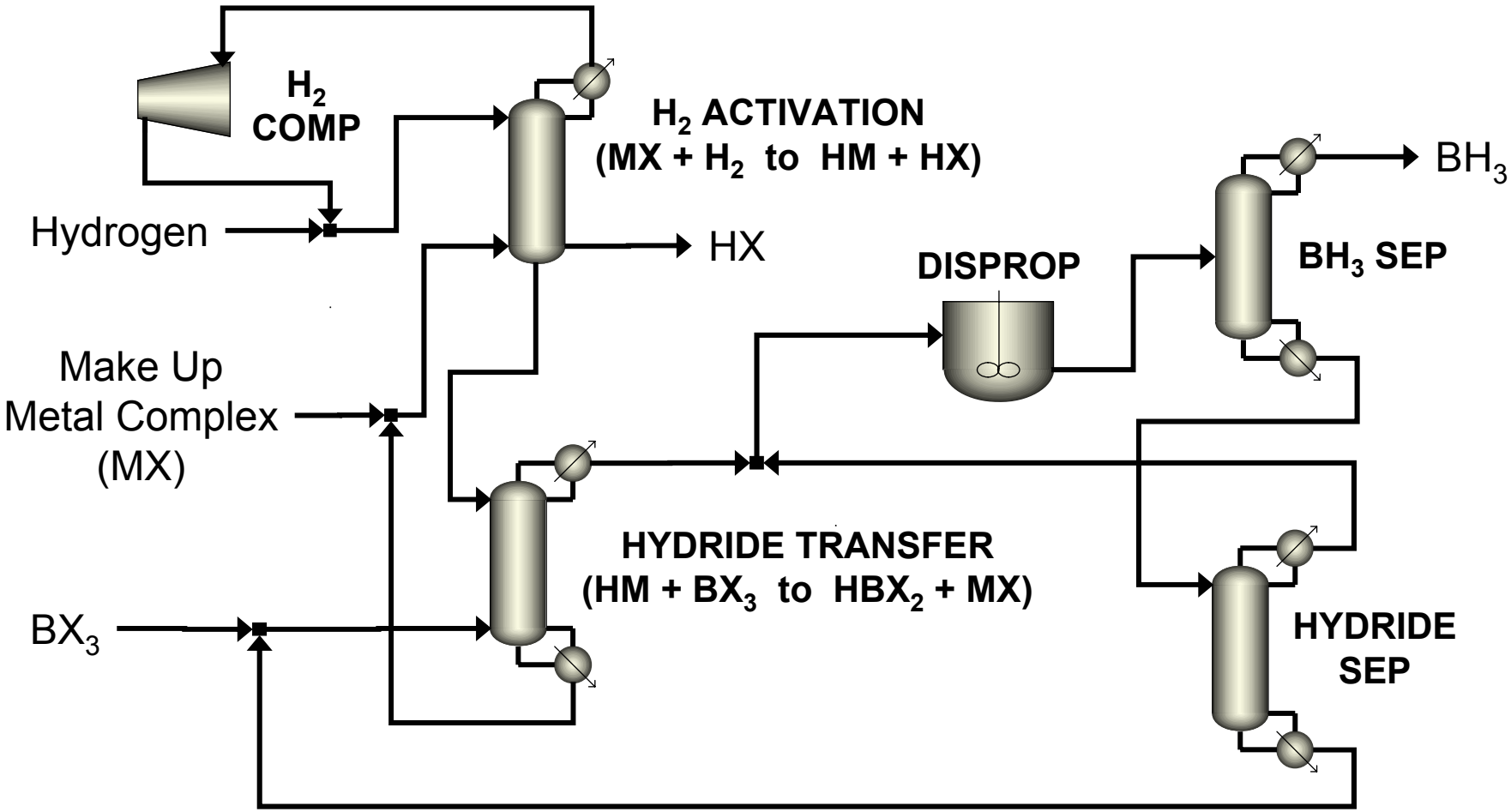
pK_a: $HX \leftrightarrows H^+ + X^-$

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 using scaffolds or by development of hybrid materials (LiAB)
  - Method for foam suppression discovered
    - Can now pursue solids handling
    - 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 flow sheets have identified several gaps
- Milestones on track & Phase 2 now underway
- Additional details available at Poster STP-3

Future Work

- Release
  - Additional focus on materials within the IPHE project: 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) and understanding efficiency/cost
  - Helping LANL, Penn by matching PNNL reduction strategy with their chemistries

Team & Collaborators

Tom Autrey
Don Camaioni
Scot Rassat
Abhi Karkamkar
John Linehan
Wendy Shaw
Dave Heldebrant
Dan Dubois
Richard Zheng
Jun Li
Mike Mock
Jerry Potter
Daiwon Choi

Chemicals COE

Los Alamos NATIONAL LABORATORY EST.1943

Penn University of Pennsylvania

UC DAVIS University of California

The University of Alabama

Rohm and Haas

University of Washington

Borax

IPHE

The University of Birmingham

NUS National University of Singapore

Industrial Research Limited

ISIS

Los Alamos NATIONAL LABORATORY EST.1943

University of Oxford

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