



PNNL Research as Part of the DOE Chemical Hydrogen COE

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**Pacific Northwest
National Laboratory**

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

DOE Hydrogen Program

Annual Merit Review

May 2007

Project ST-28

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Overview



Timeline

- Project Start: 3-15-05
- Project End: 9-30-09
- Complete: ~40%

Budget

- FY06: \$1200K
- FY07: \$1700K

Barriers Addressed

- System weight & volume for 2010
- H₂ release rate
- Thermal management
- Fuel cost: regeneration

Partners





Objectives



- Investigate chemicals that promise to meet DOE goals
 - Storage density → RELEASE (pathways/thermodynamics)
 - H₂ release rate → RELEASE (kinetics)
 - Fuel cost → REGENERATION
- Principal focus on solid ammonia borane (AB)
 - 19.6 wt%, 0.16 kg/L H₂ on a material basis
 - 13.1% quantitatively demonstrated and working to higher levels
- Coordinate efforts Center-wide on engineering



Team & Collaborations



- PNNL Team: T. Autrey, D. Camaioni, S. Rassat, J. Linehan, W. Shaw, D. Dubois, D. Rector, D. Heldebrant, A. Karkamkar, K. Rappe, R. Zheng, D. Caldwell, J. Li, L. Li, X. Li
- Center Collaborations:
 - Ammonia Boranes: LANL, Penn, UW, Alabama
 - Engineering: Rohm & Haas, Millennium Cell, LANL
 - Fuel Stability: Rohm & Haas
 - Fuel Regeneration: LANL, Rohm & Haas, Penn, UC Davis, Alabama
 - Catalysis: LANL, Penn, UW
 - Computational Chemistry: Alabama
- IPHE Collaborators: Oxford University, Industrial Research Limited, National University of Singapore, University of Birmingham, Rutherford Appleton Labs, LANL
- Additional international collaboration through IEA Task 22
- Environmental Molecular Sciences Laboratory
 - Computational Chemistry Grand Challenge in Hydrogen Storage
 - High Field NMR Facility

Collaboration is critical to meeting Center objectives

Approach

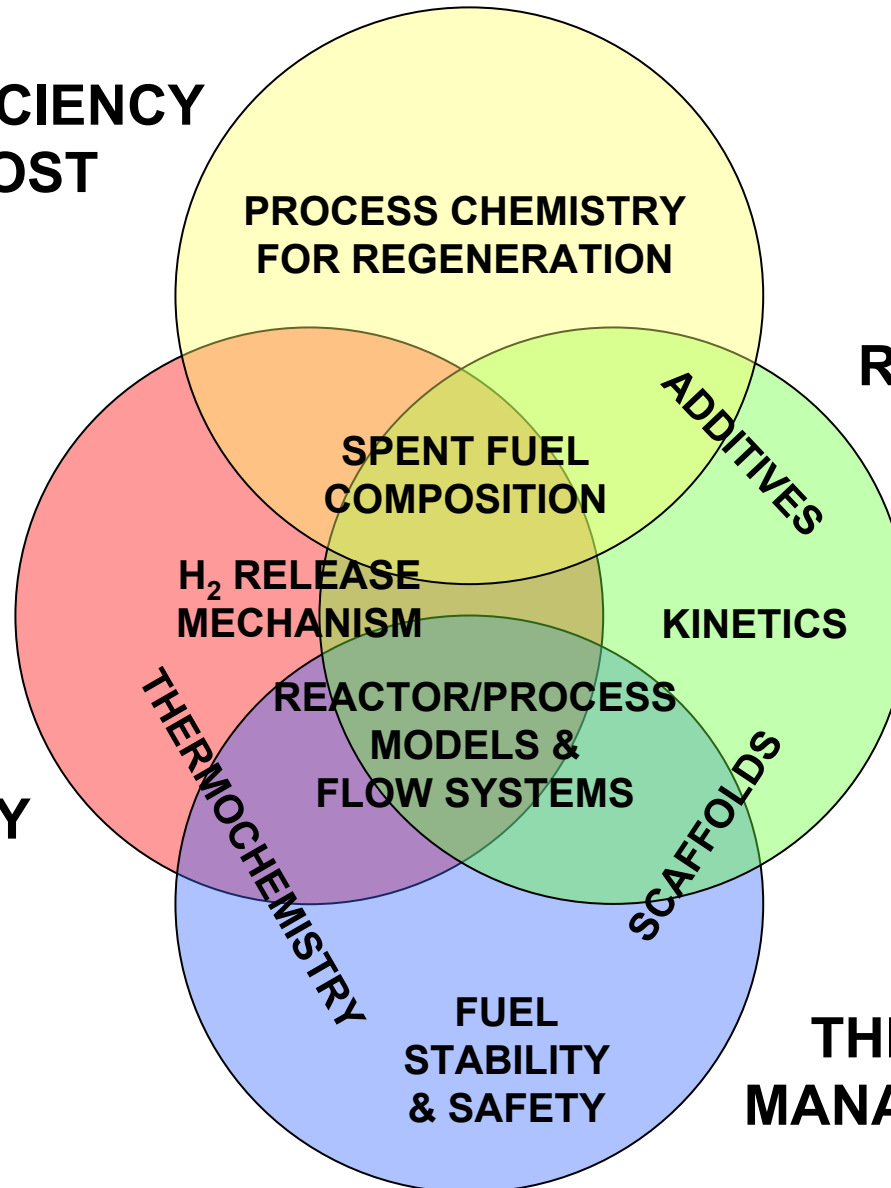
- **Release**
 - Maximize H₂ from fuel to obtain high capacity
 - Maintain balance with spent fuel → need a composition that is regenerable
 - Different approaches to control release and obtain high rates
 - Thermally driven release
 - Additives
 - Scaffolds
 - Understand the impact of working with exothermic release → safety
- **Regeneration**
 - Minimize energy and cost
 - Determine best route for digestion of solid spent fuels
 - Determine how to economically reduce boron centers
- **State-of-the-art scientific instrumentation and computational chemistry tools**
 - High Field NMR Facility
 - TGA/DSC - thermochemistry
 - Spectroscopic tools: Raman, IR, XAFS, others
 - High resolution X-ray diffraction
 - Molecular Science Computing Facility (MSCF)
- **Consider the system: use engineering tools to help direct research activities and identify pitfalls**
 - Component & process models
 - Semi-continuous & continuous bench-scale investigations

**Data being collected for Center
down-selection process at the end of FY07**

Approach: Solid AB

**ENERGY EFFICIENCY
& FUEL COST**

CAPACITY

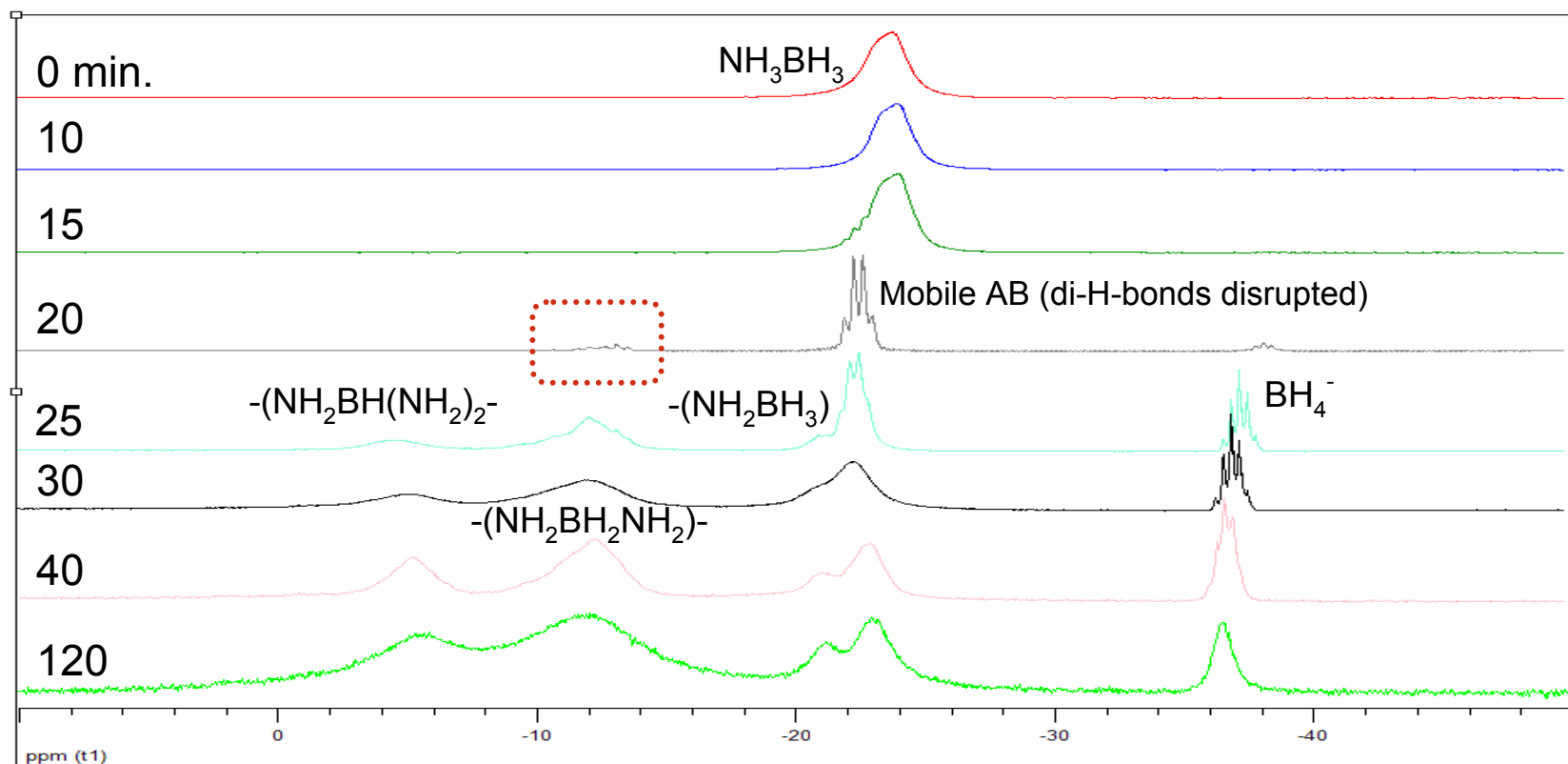


Progress

- Release
 - Now understand the mechanism for the onset of release
 - Series of experiments with high field ^{11}B NMR
 - Confirmed nucleation and growth mechanism
 - Diammoniate intermediate is key to release
 - Mechanism valid up to $\sim 120^\circ\text{C}$
 - Identified additives that accelerate release
 - Shown that AB is stable at $50/60^\circ\text{C}$ and that impurities have a large impact on release
 - Explored higher loading in silica MCM-41 scaffolds
- Regeneration
 - Demonstrated complete digestion of solid spent fuel
 - Theory used to identify better digestion approaches
 - Theory used to build case for reduction approaches
- Engineering Assessment
 - Used bench scale kinetics to understand impact of 2010 rate requirement on reactor dimensions
 - Preliminary consideration of fuel morphology indicates capacity targets likely within reach

800 MHz ^{11}B NMR: Solid AB

Neat AB: In situ @ 88°C

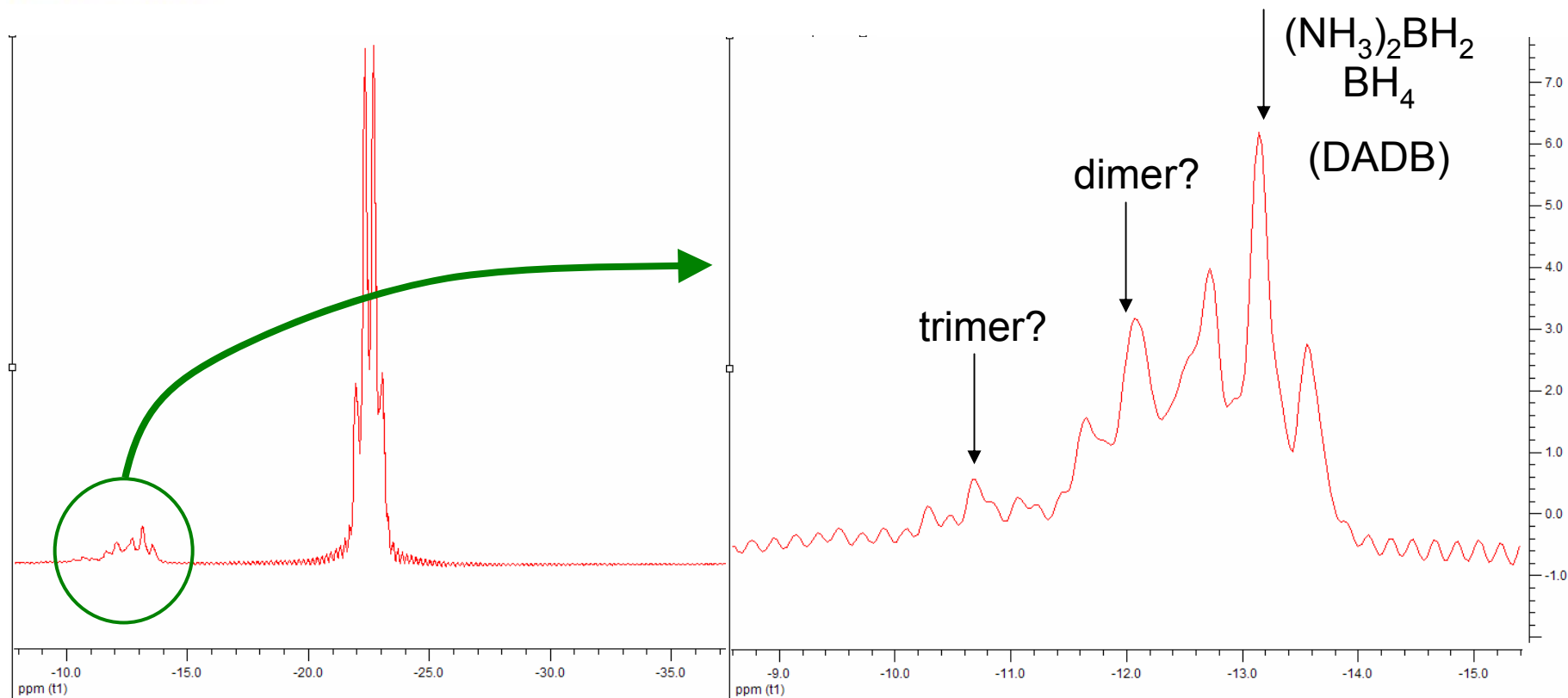


- Peaks sharpen at 20 min. indicating mobile phase
- Feature at $-(10-15)$ ppm is key to understanding mechanism

PNNL: W. Shaw, T. Autrey, J. Linehan

Impact: NMR teaches rate enhancement approaches

Transition from Nucleation to Growth



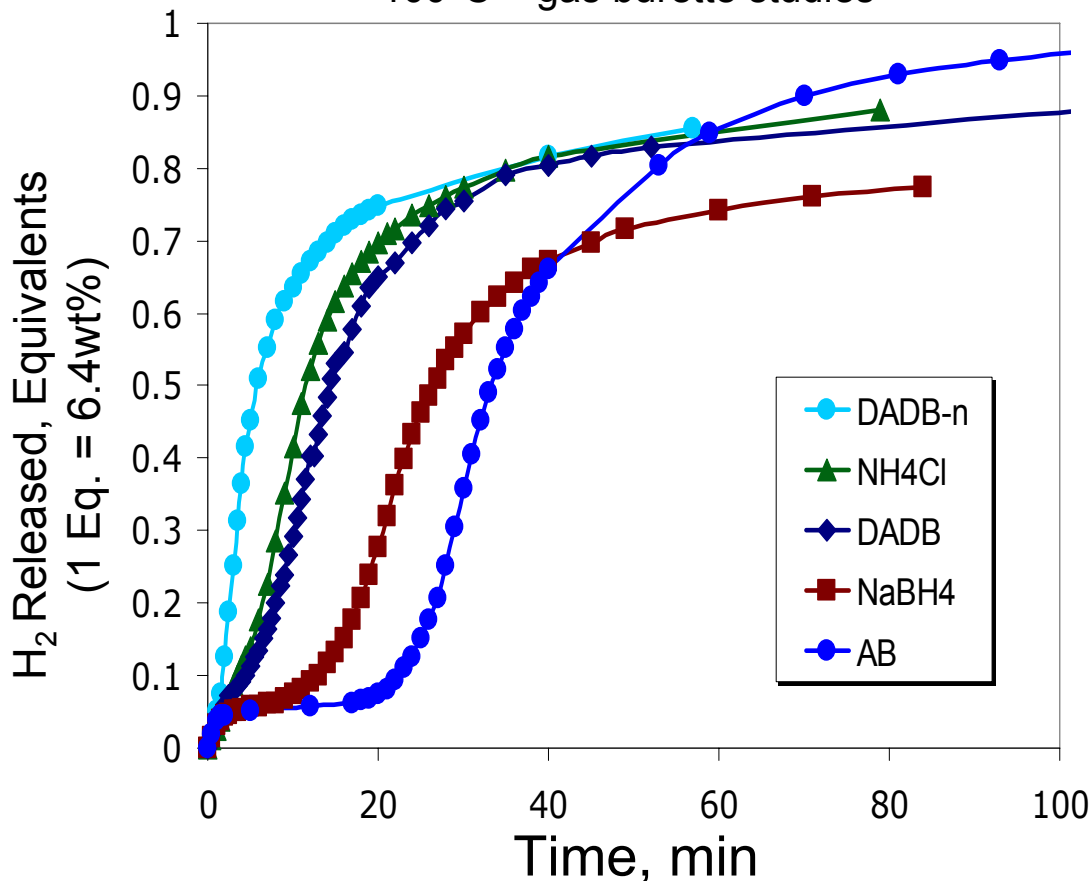
- Multiple triplets indicates series of $-\text{BH}_2-$ in slightly different chemical environments: oligomers nucleated by DADB
- DADB is the reaction initiator

PNNL: W. Shaw, T. Autrey, J. Linehan

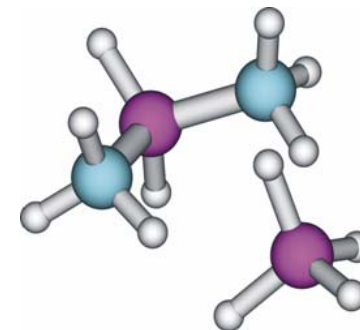
Key result: DADB is key to increasing rate

Additives Increase Release Rate

100°C – gas burette studies



DADB



- Additives reduce the induction period
- Neat DADB → fastest kinetics
- BH_4^- & NH_4^+ improve kinetics
- NH_4Cl is slightly better than DADB at 5% loading
- Acidic character appears to be important for the additive → consistent with mechanistic work

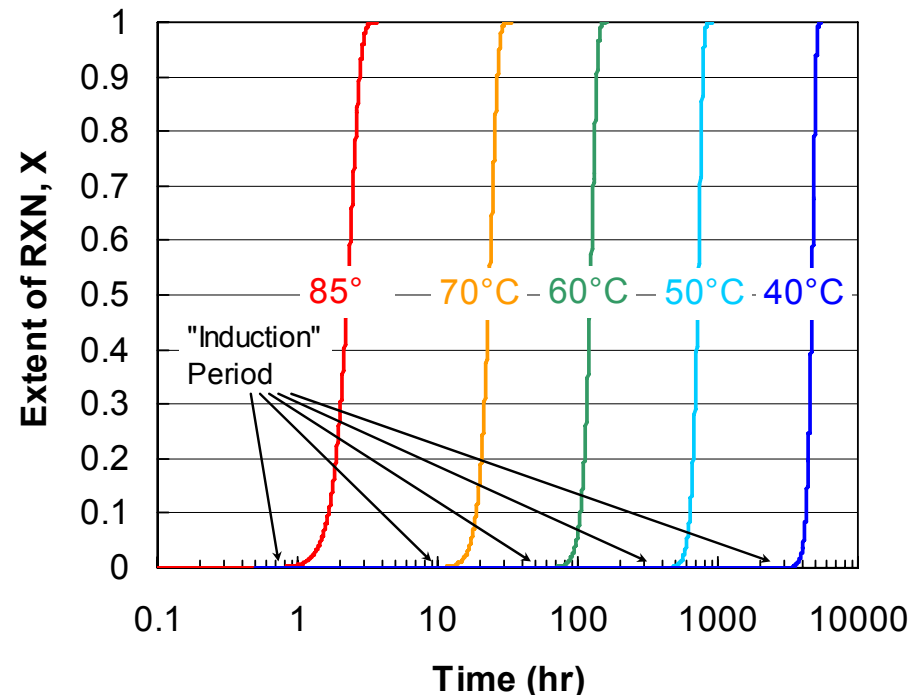
PNNL: D. Heldebrant, T. Autrey

Key result: additives to AB formulation accelerate release

- DOE target for 2015: fuel needs to be stable at 60°C
- Solid ammonia borane shows an induction period before release
- Isothermal DSC data [Wolf *et al.*, *Thermochimica Acta* **343**, (2000) 19] can be used to extrapolate release trends to lower temperatures
- Adiabatic assumed as a worst case
 - Fuel predicted to be stable for ~ 100 hrs. at 60°C
 - Greater stability at lower T

Avrami Kinetics

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

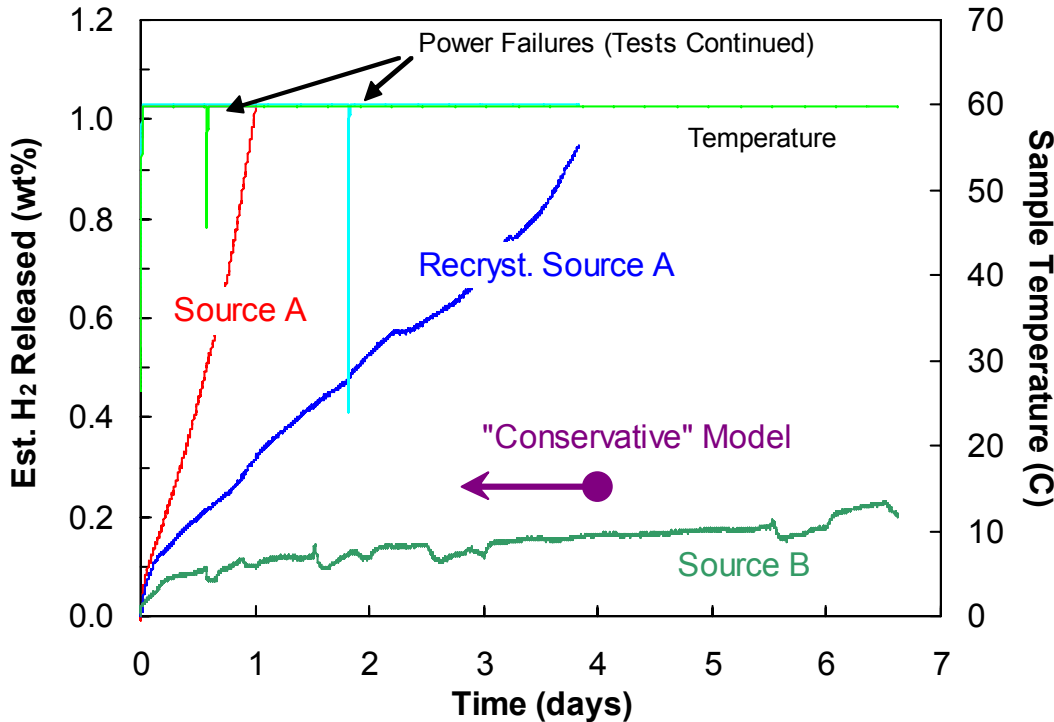


PNNL: S. Rassat, T. Autrey

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

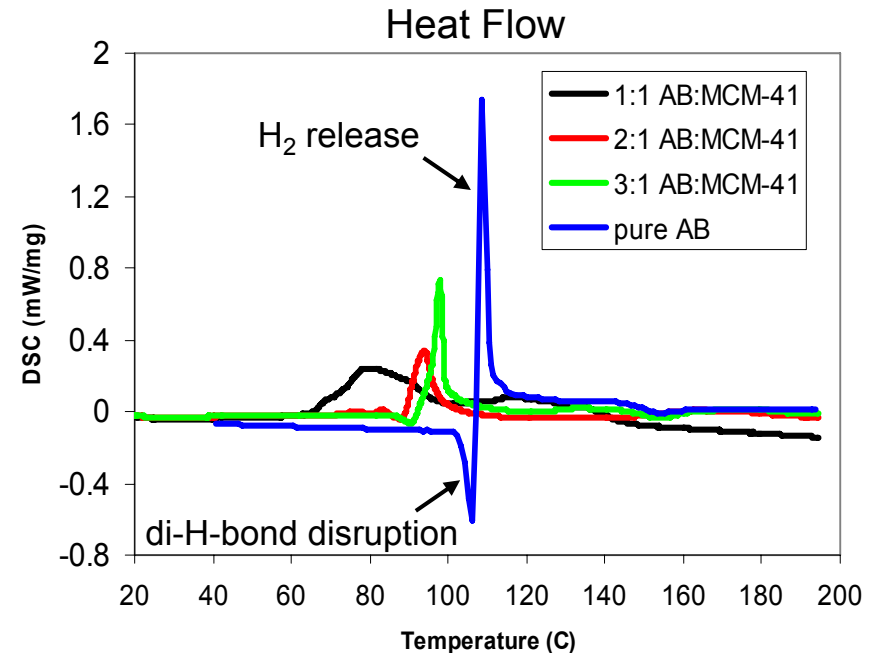
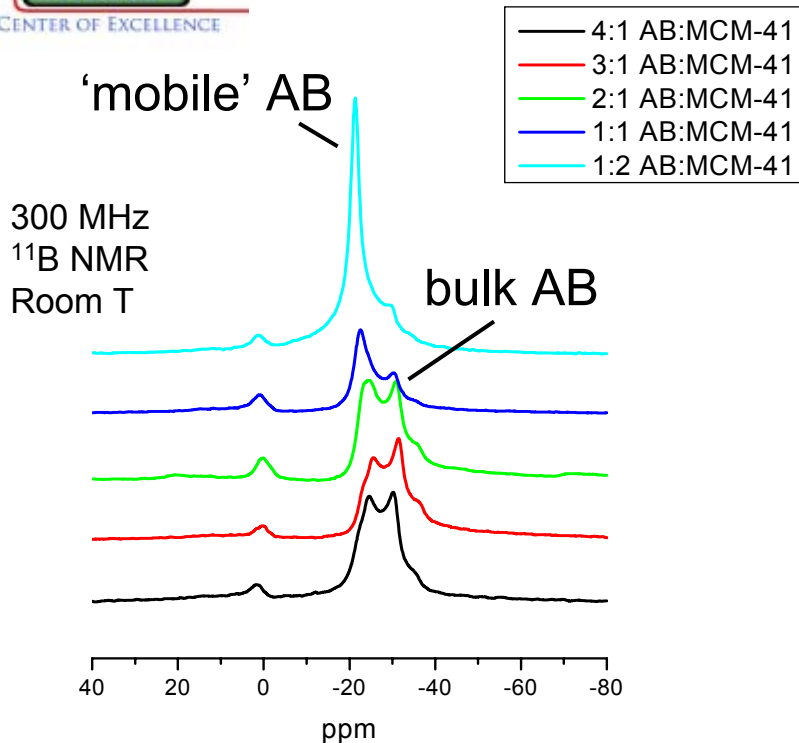
Measured Stability at 60°C

60°C, Two AB Sources



- Solid ammonia borane
 - Source A unstable
 - Source B stable
- Source B had a significantly higher purity than source A
- If source A is dissolved and recrystallized, it becomes significantly more stable
- Adiabatic hold experiments indicate that the modeling approach was conservative within the range of formulations examined

Scaffolds: Higher AB Loading



- ^{11}B NMR and DSC suggest di-H-bonds are disrupted at lower temperature
- 1:1 AB to scaffold releases hydrogen at 50°C
- Higher AB loading may offer best trade off between tuned thermodynamics and fuel stability

PNNL: A. Karkamkar, W. Shaw, T. Autrey

Key result: scaffolds allow tuning of thermodynamics and kinetics

Regeneration of Ammonia Borane

- RECLAMATION
- Spent fuel is off-boarded at fueling station
- Transported to large-scale regeneration facility

- DIGESTION (& DISPROPORTIONATION)
- First step is to dissolve the fuel
- Fuel has to be digested to allow chemical manipulation

- REDUCTION & DISPROPORTIONATION
- Reduction is required to get H₂ back into the spent fuel
- Disproportionation allows recovery of ammonia borane

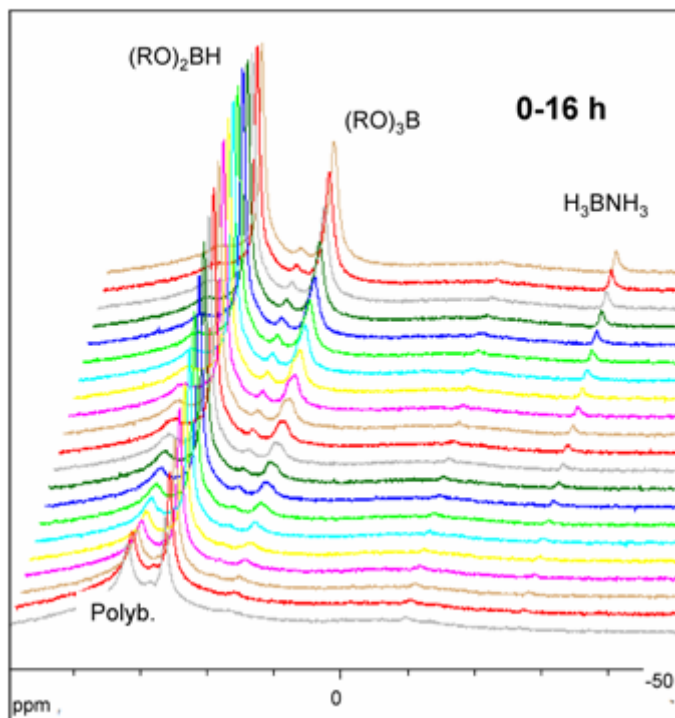
REGENERATED FUEL VIA MULTI-STEP PATHWAY

Digestion with Disproportionation

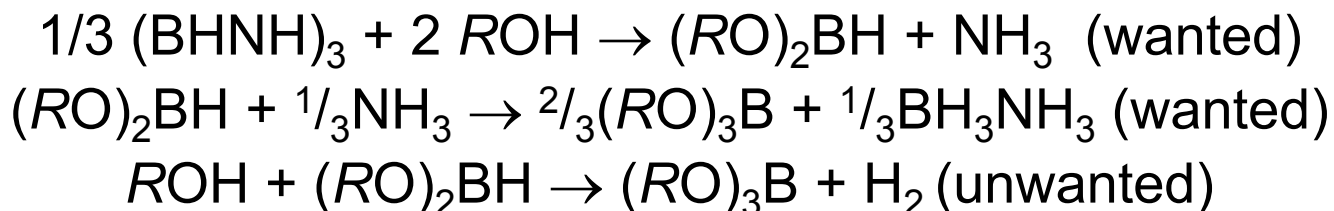
Polyborazylene
+ *t*-BuOH

Digestion in
capped vial
at room
temperature

300 MHz ^{11}B
NMR time study



- **Digestion:** *t*-BuOH digests compounds analogous to spent AB fuel
- **Disproportionation:** $\text{B}(\text{O}t\text{-Bu})_3$ and AB are formed over time from initial product
- There is competition between AB and H_2 formation
 - MeOH favors H_2
 - *t*-BuOH favors AB

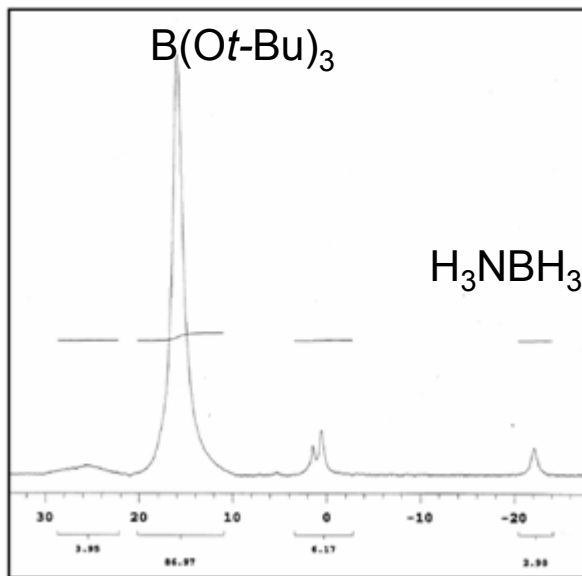


PNNL: D. Heldebrant, J. Linehan, D. Camaioni

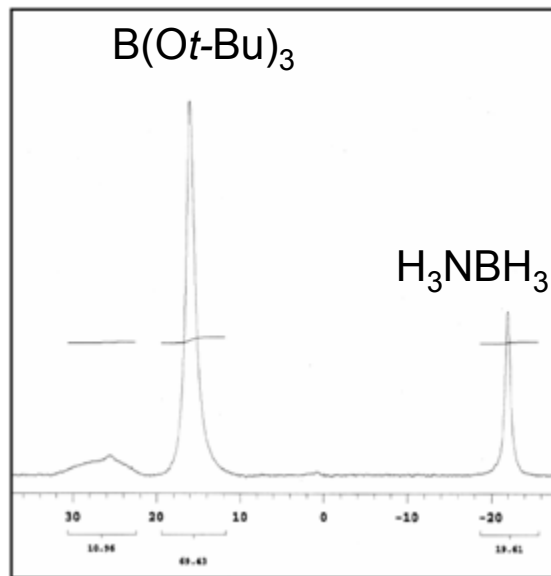
Impact: B-H recovered through one pot digestion and disproportionation

Digestion: Effect of Ammonia Addition and Alcohol Substitution

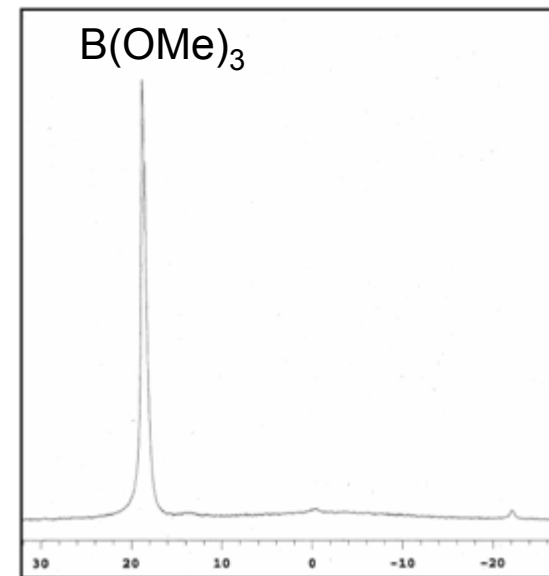
3 equiv. *t*-BuOH
36 h.



3 equiv. *t*-BuOH
211 psi NH_3 , 12 h.



3 equiv. MeOH
211 psi NH_3 , 12 h.

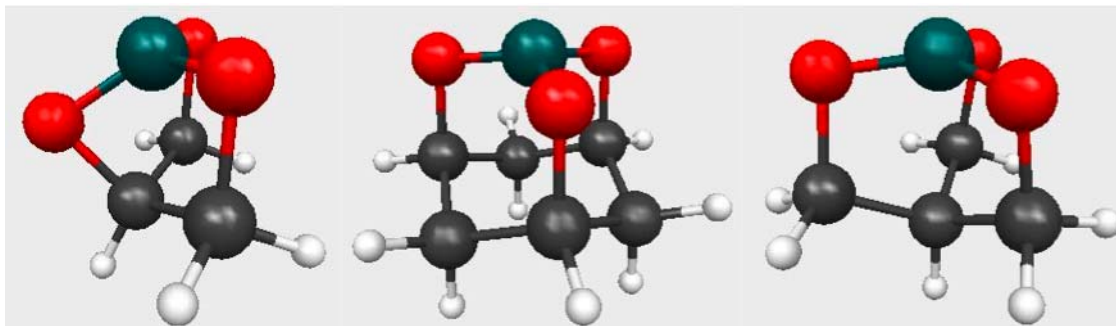


- 6-fold increase in B-H recovery with NH_3 overpressure
- MeOH gives little NH_3BH_3 → B-H loss dominates
- $B(Ot-Bu)_3$ co-product → B-OR bonds may be difficult to reduce

PNNL: D. Heldebrant, J. Linehan, D. Camaioni

Impact: ammonia speeds digestion & increases yield of NH_3BH_3 6-fold

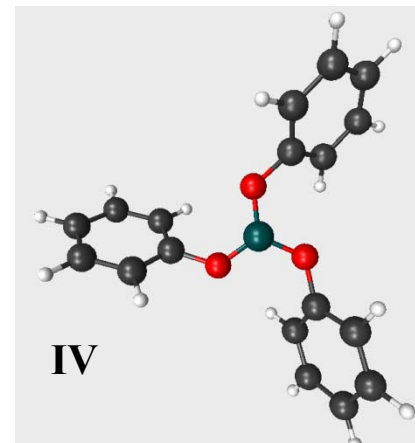
Theory: A Guide to the Best Digestion Strategy



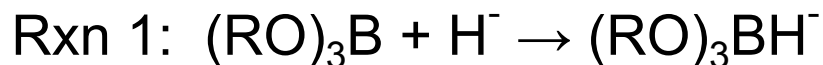
I

II

III



IV



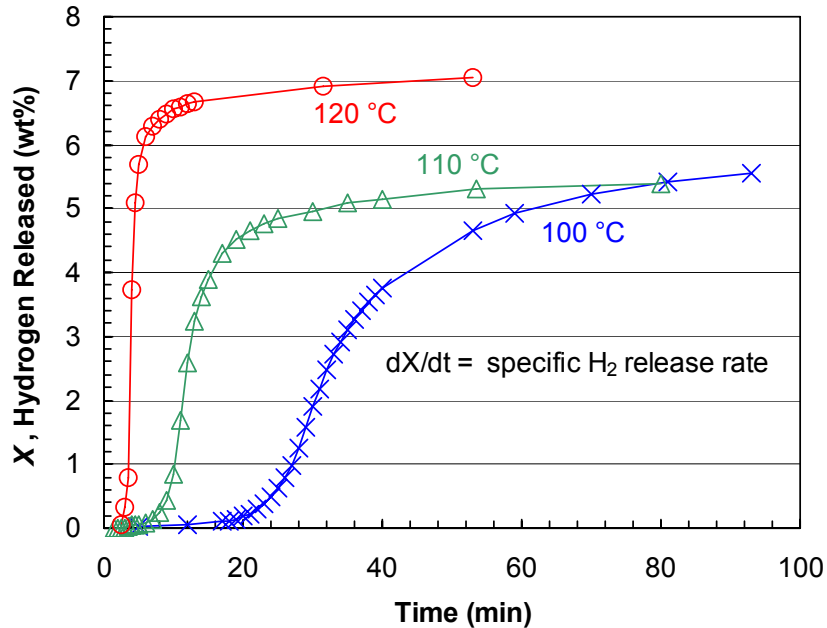
Alkyl	B-O (Å)	O-B-O	B-O-C	$-\Delta H_1$
Glyceryl, I	1.43, 1.39	113°, 122°	82°, 93°	115
Cyclohexa-1,3,5-triyl, II	1.39	118°	101°	100
Methanetrimethyl, III	1.39	118°	100°	96
Triphenyl, IV	1.37	120°	126°	87
Trimethyl	1.37	120°	121°	51

PNNL: D. Camaioni, J. Li

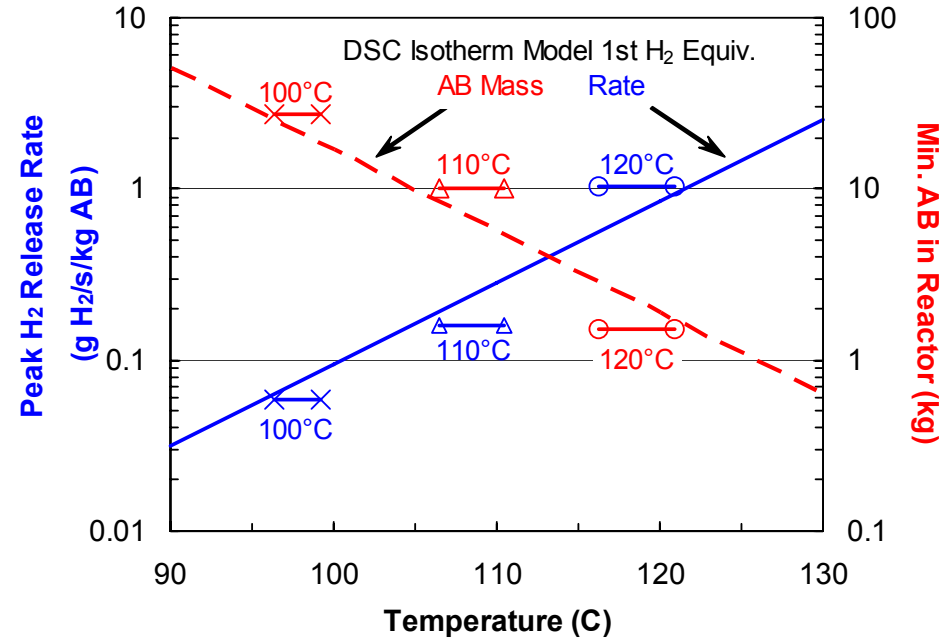
Impact: strained B-O bonds are 36-64 kcal easier to reduce than B(OMe)₃

Engineering Assessment Toward Meeting the DOE Rate Targets Bench Scale Kinetics → Reactor Size

Neat AB, Gas Burette Tests



Data vs. DSC-Based Model

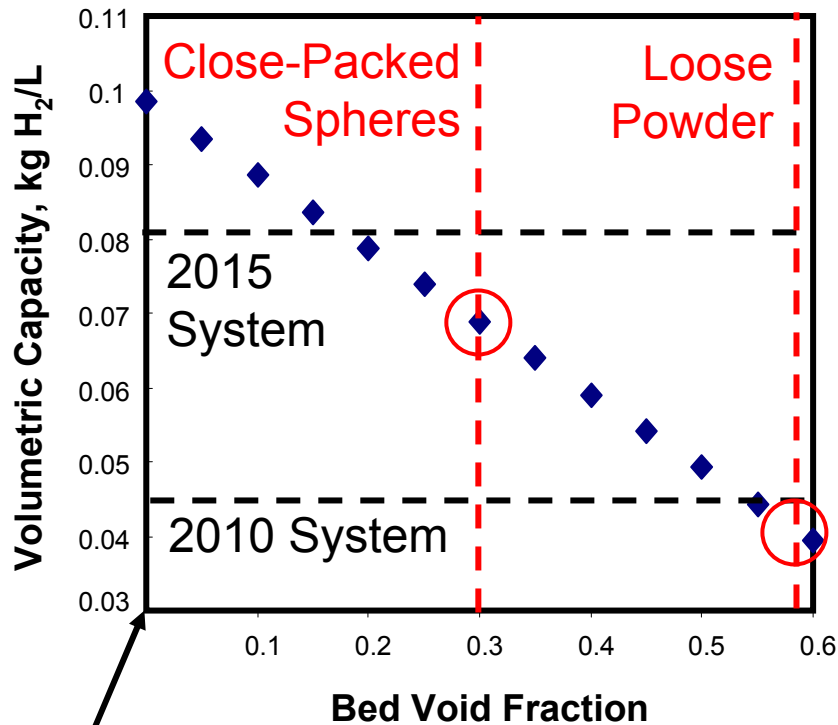


PNNL: S. Rassat, D. Heldebrant, T. Autrey

Impact: DOE rate target can be achieved with modest sized reactor

Engineering Assessment Impact of Solid Fuel on Capacity

2 Equiv. H₂ from AB (13.1 wt%)



Single
Crystal

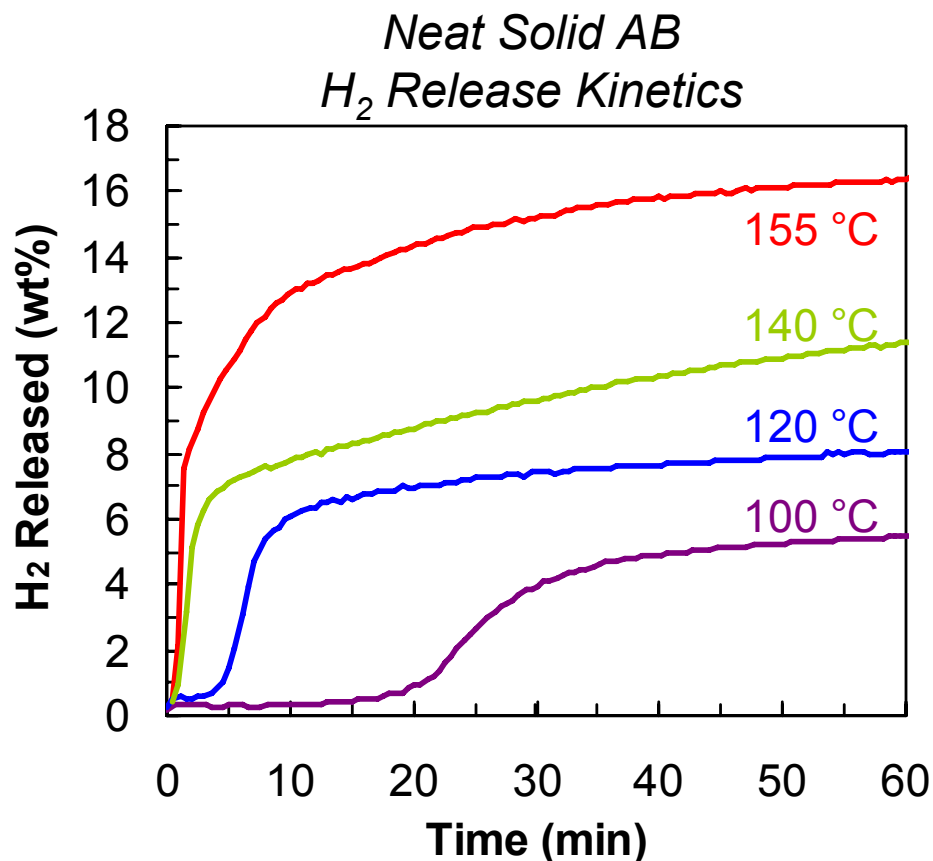
- Loosely packed AB powder cannot make the 2010 system target
- 2010 system target may be attainable with pellets
 - How is release impacted by pellet size?
 - What packing density is realistic?
- 2015 system target is not attainable with a pellet-based approach
- Game changers:
 - Ultra-low voidage approach
 - More H₂ from AB

PNNL: S. Rassat, T. Autrey, A. Karkamkar

Volumetric capacity target looks possible with an engineered morphology

Higher Temperature Preliminary Data

- New gas burette apparatus allows release at higher temperature
- Working to higher temperature to further increase rate and capacity
- Wt% > 16% H₂
- Max rate > 3 gH₂/s/kg AB
- Virtually no induction period observed at higher temperatures



D. Heldebrant, S. Rassat, T. Autrey

Key result: higher temperature could be the key to capacity & rate

Future Work: Release

- Continue to drive up Capacity
 - Higher temperature → > 2 equivalents (mechanism still poorly understood)
 - Volumetric: fuel morphology & low voidage formulations
- Continue to drive up Rate
 - Higher temperature → faster kinetics
 - Additives – enhance release and maintain stability
 - Need to understand kinetics of H₂ release after 1st equivalent
- Quantitative measurement of H₂ purity
- Scaffolds: different surface chemistry to tune thermodynamics, kinetics while maintaining fuel stability
- Reactor and process concepts for solids: keep working toward evaluation based on systems rather than materials
 - Apparatus being assembled for continuous processing
 - Examine impact of engineered solids on release
 - Component and process model development

Regeneration: Future Work

- Drive to better efficiency
- Develop strategies that destabilize the bonds formed during digestion and offer good access to the B center for reduction
 - Theory indicates destabilization using polyols & phenols
 - Need to look at -SH in addition to -OH digestions
- Incorporate reduction pathways
 - Rohm & Haas efficiency analysis has shown that Zn may be an economical metal route to sodium borohydride
 - PNNL synthesizing ZnH_2 in support of experimental program
 - PNNL will examine ZnH_2 for reduction of spent ammonia borane
 - Theory driving renewed interest in transfer hydrogenations
 - New pathway proposed by Dan Dubois at PNNL
 - Activates H_2 for reduction reactions
 - Theory suggests reduction of borate esters feasible
 - Use on B-O bonds directly or for regeneration of other hydrides
- Engineering analysis
 - Conceptual design & preliminary flow sheeting
 - Efficiency & cost analyses

Future Regeneration Catalytic Activation of H₂ for Reduction

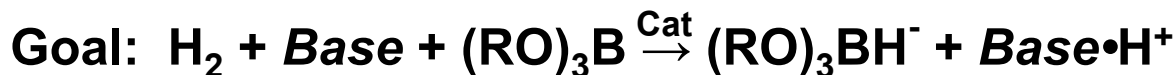
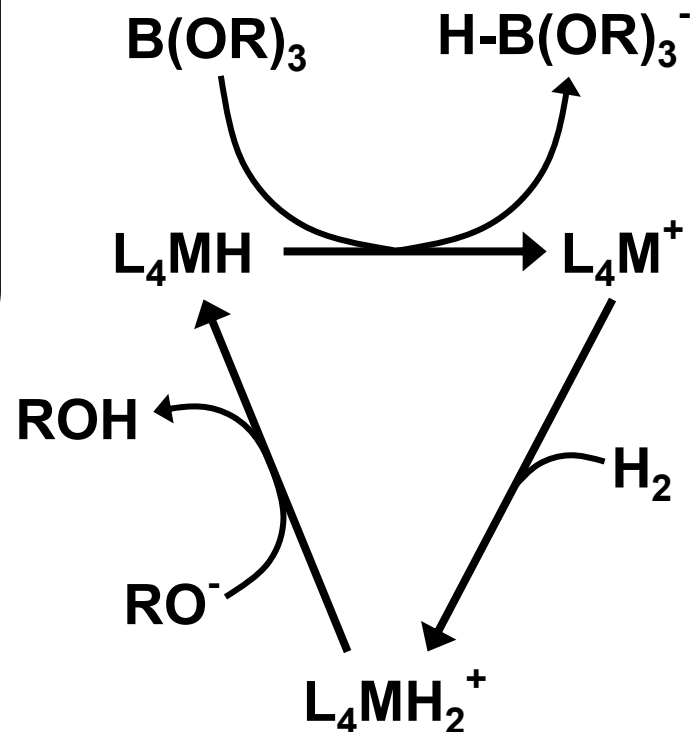
Dubois *et al.* *Organometallics* (2006)



Theory: $\Delta G = -14$ kcal/mol



- Cannot reduce with H₂ alone
- Couple catalysis to acid-base chemistry to drive reaction
- Working on one pot reaction



PNNL: D. Dubois, J. Linehan, D. Camaioni, D. Heldebrant

Impact: route demonstrated by Dubois *et al.* should reduce B(OPh)₃

Summary: Release

- Neat AB appears to be the front runner at present
 - Mechanism of release is pretty clear for 1st Equivalent
 - Temperature can be used to control rate
 - Demonstrated release of up to 16+ wt% (preliminary) for material
 - Need more kinetics studies on 2nd+ equivalents
 - Fuels can be formulated for long term stability at 60°C (2015 target)
- Additives have been identified that greatly accelerate the rate of release
 - Need to determine if there are additives that allow increased rate at release temperature, but stable fuel at 60°C
 - Scaffolds are still of great interest, but additional work needs to be done to be sure stable fuels are possible
- Simple engineered forms have potential to meet the 2010 gravimetric and volumetric targets for a system
- Based on the 2010 maximum rate target, reactor sizes look to be reasonable



Summary: Regeneration



- Shown how theory is guiding digestion and reduction work at PNNL
 - Need to destabilize borate ester co-products and look at $-SH$
 - Two ideas on reduction pathways to be examined over the next year
- Digestion & disproportionation with B-H recovery has been demonstrated
- Ammonia overpressure dramatically impacts B-H recovery
- Engineering analysis will start now that regeneration routes are emerging

Summary Table (Solid Ammonia Borane)

Temp (°C)	Weight % H ₂		Vol. Cap. (kg/L) (loose powder)	Max. Rate (gH ₂ /s/kg)	kg AB in Reactor for 2010 rate
	2006	2007			
60 (1:1 Scaffold)	3.2	3.2	---	---	---
86.5	5.5	5.5	---	---	---
120	6.5	7	0.021	1	2
140	---	>13	0.039	1.8	1
155	---	>16	0.048	>3	0.8

All numbers provided above are MATERIAL values

DOE targets are based on system:

2010 Gravimetric Capacity of 6%

2010 Volumetric Capacity of 0.045 kg/L

2010 Rate of 0.02 gH₂/s/kW