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DOE Hydrogen Program

DOE Chemical Hydrogen Storage Center of Excellence

An Integrated Performance-Based Approach

STP-9

Los Alamos NATIONAL LABORATORY EST. 1943

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

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Millennium Cell

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Penn UNIVERSITY of PENNSYLVANIA

PENNSTATE 1855

Intematix

ROHM AND HAAS

UNIVERSITY OF WASHINGTON

Objectives and Approach

- Identify, research, develop, and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals, develop life cycle inventory, and demonstrate a 1 kg storage system.

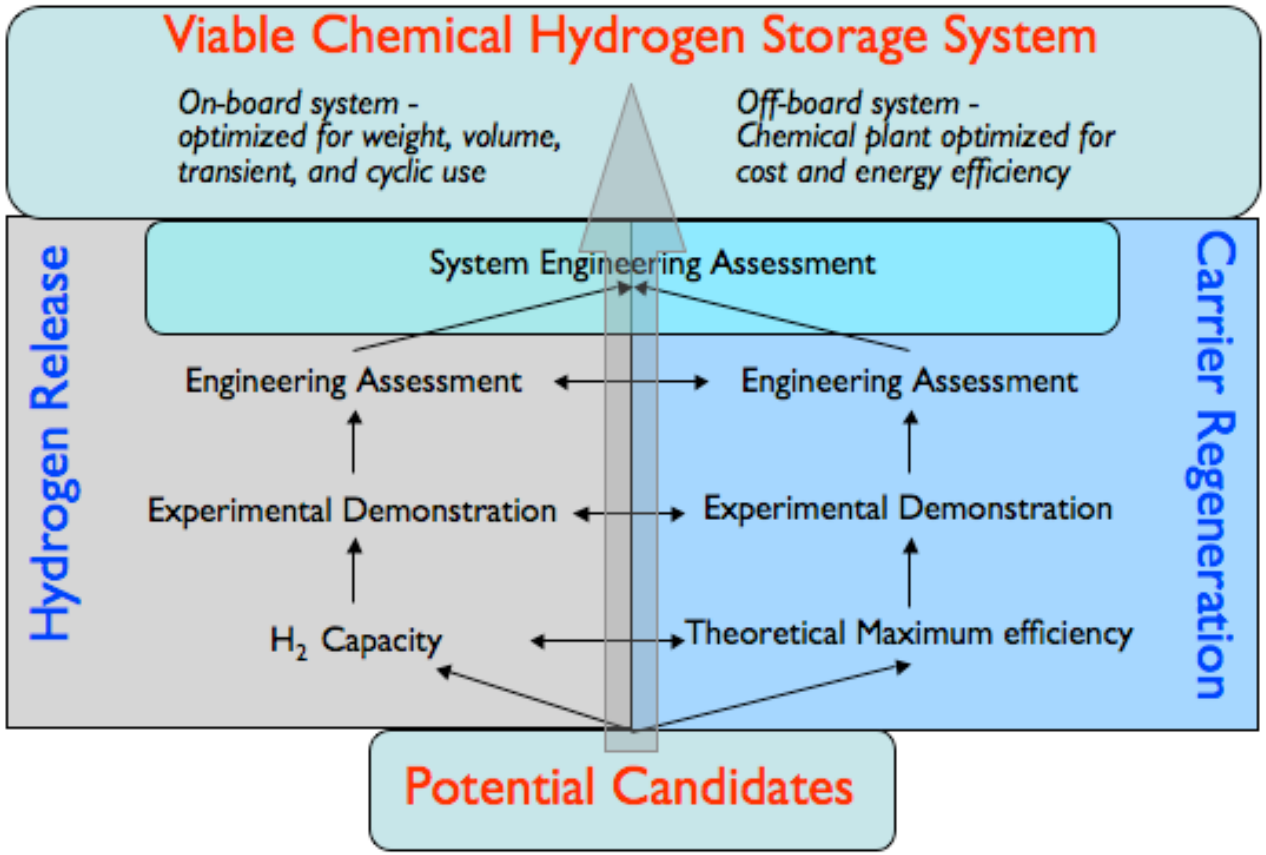
Science of Chemical Hydrogen Storage

- Capacity
  - Develop, synthesize, and test compounds with high hydrogen density and suitable energetics
  - Exploit theory and modeling for insight
- Hydrogen release
  - Control pathways to avoid unwanted byproducts
  - Elucidate mechanisms an dreaction kinetics
  - Develop and optimize catalytic processes
- Regeneration
  - Develop most energy efficient pathways
- Engineering
  - Assess concepts and systems for development

Current Center Projects

- BO to BH Engineering Guided Research
  - R&H, MCEL, PSU, Ala, PNNL, LANL
- Engineering Assessment of Hydrogen Generating Systems
  - MCEL, R&H, LANL, PNNL
- Polyhedral borane chemistry
  - Missouri, Penn
- Amine Borane Chemistry
  - Penn, U. Wash, NAU, Ala, IMX, UC Davis PNNL, LANL
- Amine Borane Systems Engineering, Safety
  - PNNL, NAU, LANL, R&H
- Organics and Coupled Reactions
  - Ala, PNNL, U. Wash., LANL
- Nanoparticles and main group hydrides
  - UC Davis, LANL
- Metal amine borane compounds (IPHE collaboration)
  - LANL, PNNL

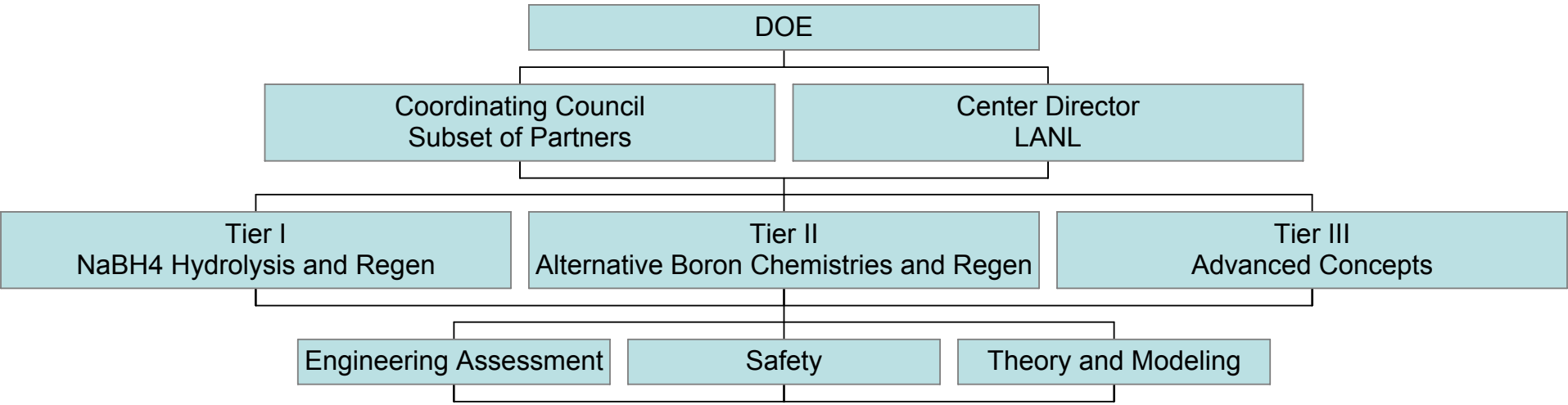
Performance-Based Approach



Center Partners

- Penn: Prof. Larry Sneddon
  - Laif Alden, Chang Yoon, Dan Himmelberger, Bill Ewing
- U. Missouri: Prof. Fred Hawthorne
  - Satish S. Jalisatgi, and Alexander V. Safronov
- Penn State: Prof. Digby McDonald
  - Sergi Colominas, Justin Tokash, Jason McLafferty, Valerie Bao, James Nollinger
- U. Alabama: Profs. Dave Dixon, Bo Arduengo
  - Masaaki Yoshifuji, Luigi Iconaru, Monica Vasiliu, Christian Schiel, Myrna H. Matus, Daniel J. Grant, Jackson R. Switzer, Jacob R. Batson, Minh T. Nguyen
- U. Washington: Profs Karen Goldberg and Mike Heineky
  - Nathan Bennette, Brandon Dietrich, Travis Hebden, Denise Méry
- UC Davis: Profs. Susan Kauzlarich, Phil Power
  - Doinita Neiner, Julia Wang, Audra Betzer, Bobby Ellis, Alex Pickering; and Prof. Alex Navrotsky, Ping Yu
- NAU: Prof. Clint Lane
  - Sharon Baker
- Rohm and Haas: Sue Linehan
  - F. J. Lipiecki, A. A. Chin Kebede Beshah, Shih-Ying Hsu, Puja Jain. Leo Klawiter, Steve Maroldo, Joe Magee, Steve November, Gary Van Sciver, John Yamamoto, Larry Guilbault, Innochem Inc., Duane Mazur, Electrolytica Inc.
- MCEL: Ying Wu, Oscar Moreno
  - Jeffrey Ortega, Xiaolei Sun, Rick Mohring, Mike Kelly, Todd Randall, Roxanne Spencer
- Intematix: Xiao-Dong Xiang
  - Wei Shan, Jonathan Melman, Guanghi Zhu
- Rio Tinto: Dave Schubert
  - Jonathan Owen
- PNNL: Chris Aardahl
  - 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
- LANL: William Tumas
  - R. Tom Baker, Anthony Burrell, John Gordon, Neil Henson, Michael Inbody, Kevin Ott, Troy Semelsberger, Frances Stephens, David Thorn, Ben Davis, Himashinie Diyabalanage, Charles Hamilton, Karl Jonietz, Rich Keaton, Vincent Pons and Roshan Shrestha

DOE's Chemical Hydrogen Storage Center of Excellence

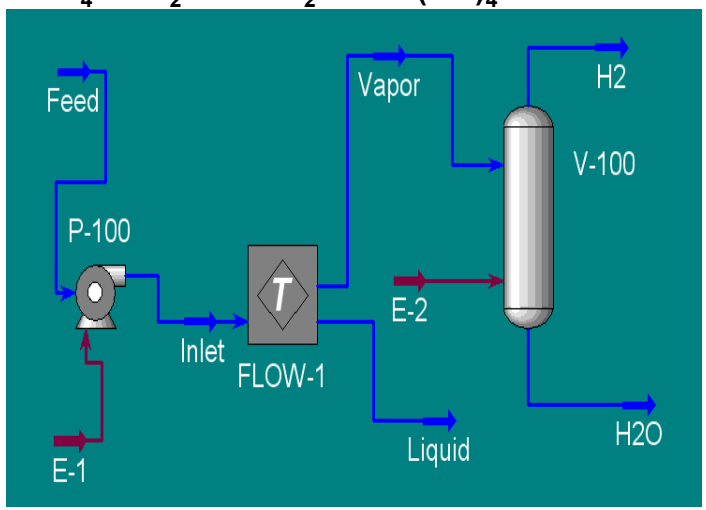


BO to BH

- Engineering-guided R&D towards 2007
  - Go/No Go Decision of Onboard Hydrogen Generation and Off-board Regeneration for Sodium Borohydride: B-O to B-H

Engineering systems assessment for onboard H_2 generation (MCEL)

$$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaB(OH)_4$$



•UniSim selected for robust treatment of electrolytes

•Data from reactor modeling can be used as parametric data for reactor module in UniSim

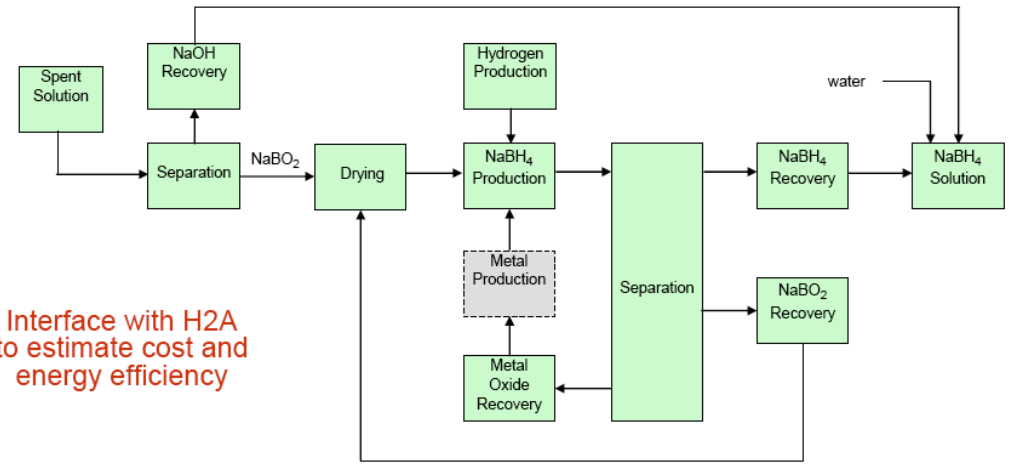
•Conditions examined: 20°C, 1140 kPa, 0.54 kmol/hr flow rate

- R&D at Penn State to demonstrate an electrochemical route for regeneration of $NaBH_4$ from borate solutions
  - Search for cathodes that don't decompose BH4-
  - Chemical modification of cathodes to bind borate
- Search for one-step reduction of borate in aqueous media at high overpotential
- Non-aqueous 2-step routes for the reduction of trimethylborate or sodium trimethoxyborohydride

Engineering systems assessment for offboard regeneration (R&H)

$$NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$$

Evaluate criteria for energy/cost efficient regeneration chemistries with energy efficiencies ≥ 60%:
Metal reduction, carbothermal, electrochemical (R&H)

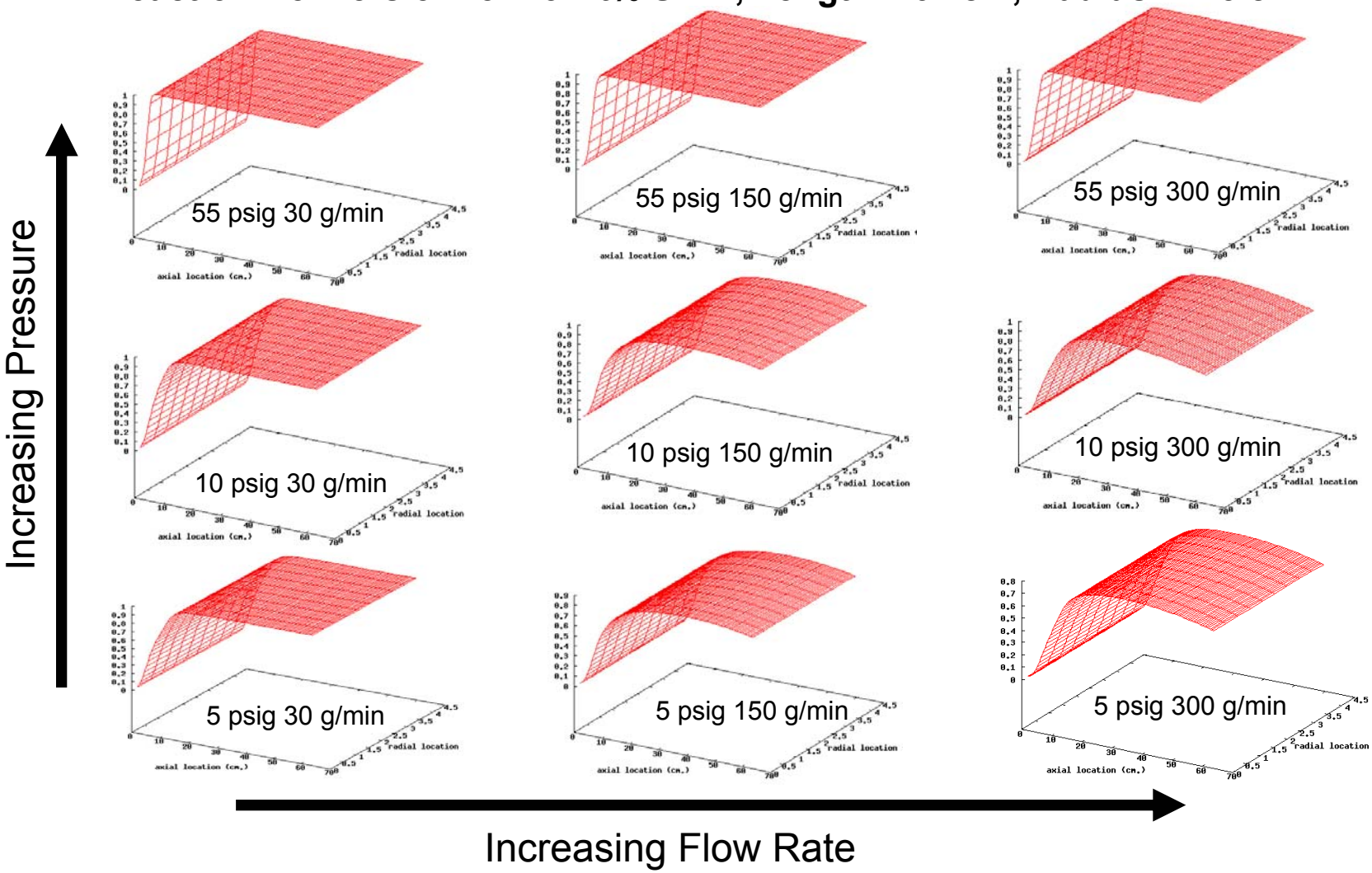


Interface with H2A to estimate cost and energy efficiency

SBH Hydrolysis Models: Reactor Performance

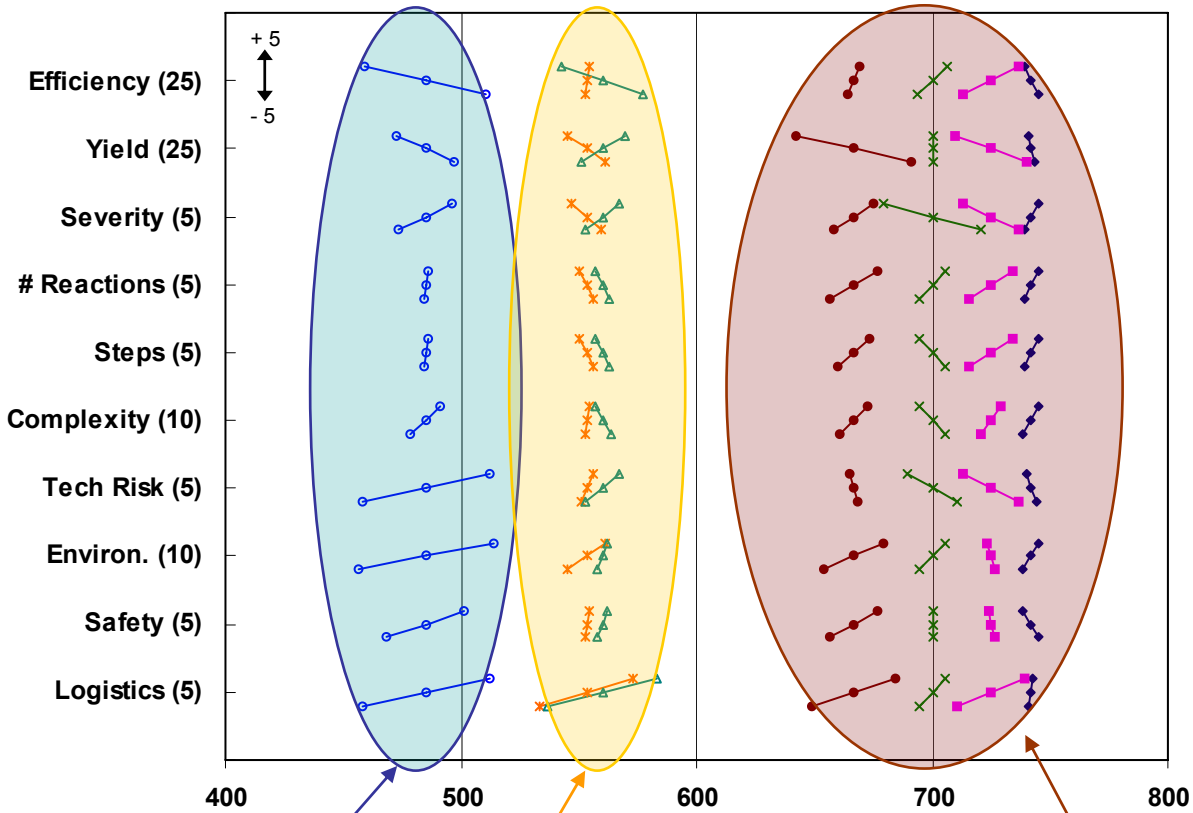
Space Velocity & Pressure

Reaction Conversion for 25 wt% SBH , Length = 62 cm, Radius = 4.5 cm



Sensitivity Analysis for SBH Offboard Regen

Variation of ± 5 in criteria weighting factor has minimal effect on rankings



Schlesinger process lowest

Borane* and metathesis paths provide only moderate improvement

Metal reduction *, carbothermal, elemental, and electrochem * paths provide highest scores

*** average**

FY07 Sodium Borohydride Go/ No-Go Decision Evaluation Criteria

DOE has commissioned an independent review panel to conduct at technical assessment of the status and progress of the sodium borohydride hydrolysis and regeneration effort. The time-phased criteria the panel will consider are:

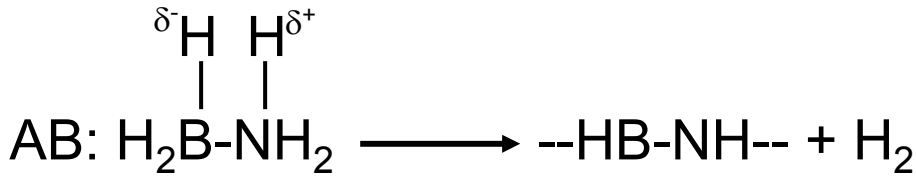
- Ability to meet 2007 DOE Technical Targets:
  - System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass) = 1.5 kWh/kg (0.045 kg H_2/kg system)
  - System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume) = 1.2 kWh/L (0.036 kg H_2/L system)
  - Storage system cost = $6/ kWh net (200 $/kg H_2)
- ≥ 60% energy efficient regeneration

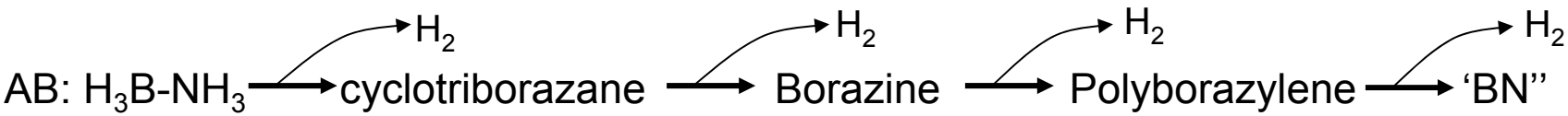
- Likelihood of meeting DOE 2010 Technical Targets:
  - System Gravimetric Capacity: Usable, specific-energy from H2 (net useful energy/max system mass) = 2.0 kWh/kg (0.06 kg H2/kg system)
  - System Volumetric Capacity: Usable energy density from H2 (net useful energy/max system volume) = 1.5 kWh/L (0.045 kg H2/L system)
  - Storage system cost = $4/ kWh net (133 $/kg H2)
  - Fuel cost (spent fuel regeneration) = $2-3/gal gas equivalent (gge) at pump.

DOEs Independent Review Panel is scheduled for early Sept.

Ammonia Boranes for Hydrogen Storage

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes, ABs, are unique in their ability to store and release hydrogen while avoiding B-O formation





	H_2 wt%, H_2 density (assumes conv. to 'BN')	properties
NH_4BH_4	24.5%, 0.2 kg-H_2/L;	Unstable > -20°C
AB: NH_3BH_3	19.6, 0.16	Crystalline solid
Cyclotriborazane: $B_3N_3H_{12}$	14.9, 0.11	Crystalline solid
Borazine: $B_3N_3H_6$	7.5, 0.06	Liquid, bp 55 °C
AT: $NH_3B_3H_7$	17.8, 0.14	Crystalline solid
MeAB: $BH_3NH_2CH_3$	8.9, 0.08 (assuming $2H_2$/MeAB)	Solid, mp 55 °C

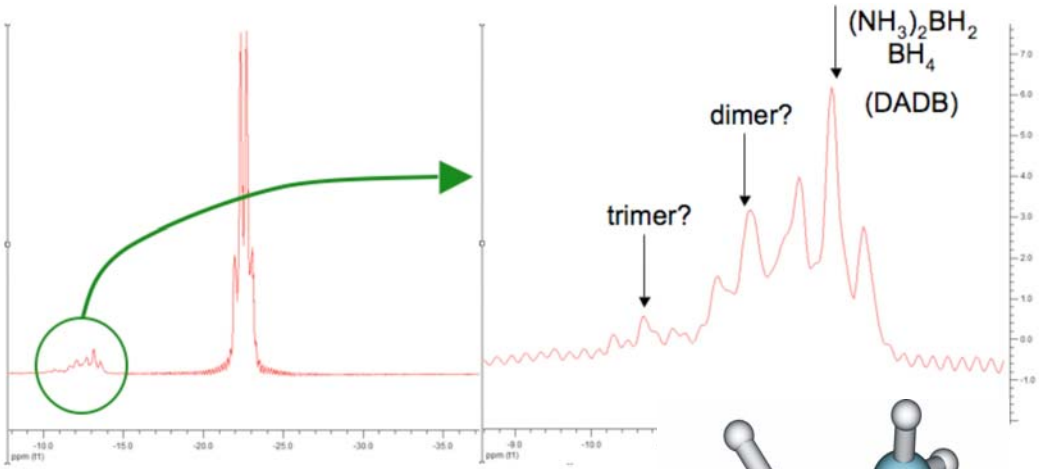
DOE Metrics: **2007** 4.5 wt %, 0.036 kg-H_2/L; **2010**: 6.0 wt. %, 0.045 kg-H_2/L; **2015**: 9.0 wt%, 0.081 kg-H_2/L

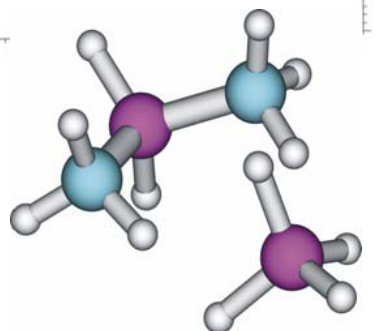
Key developments

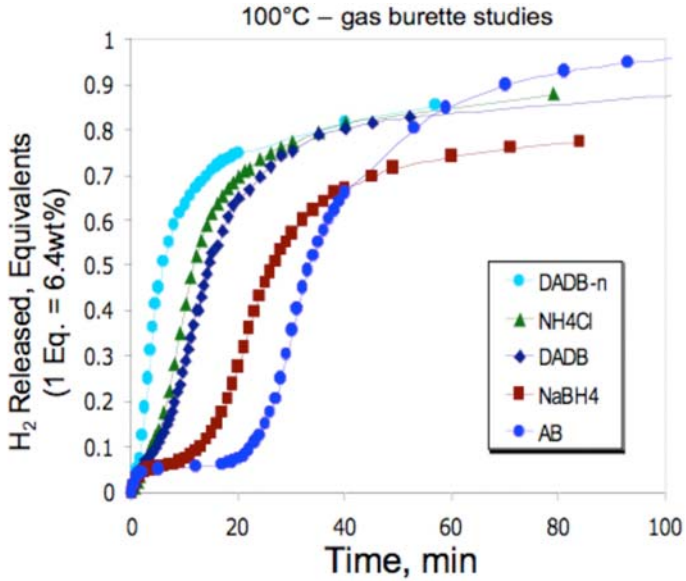
- Mechanistic understanding has led to greater extent of release, with faster rates
- Engineering assessments have led to search for liquid formulations, and higher density solids
- Large number of parameters to be explored and controlled has led to greater use of high throughput screening

Thermolytic Release of Hydrogen from Solid AB

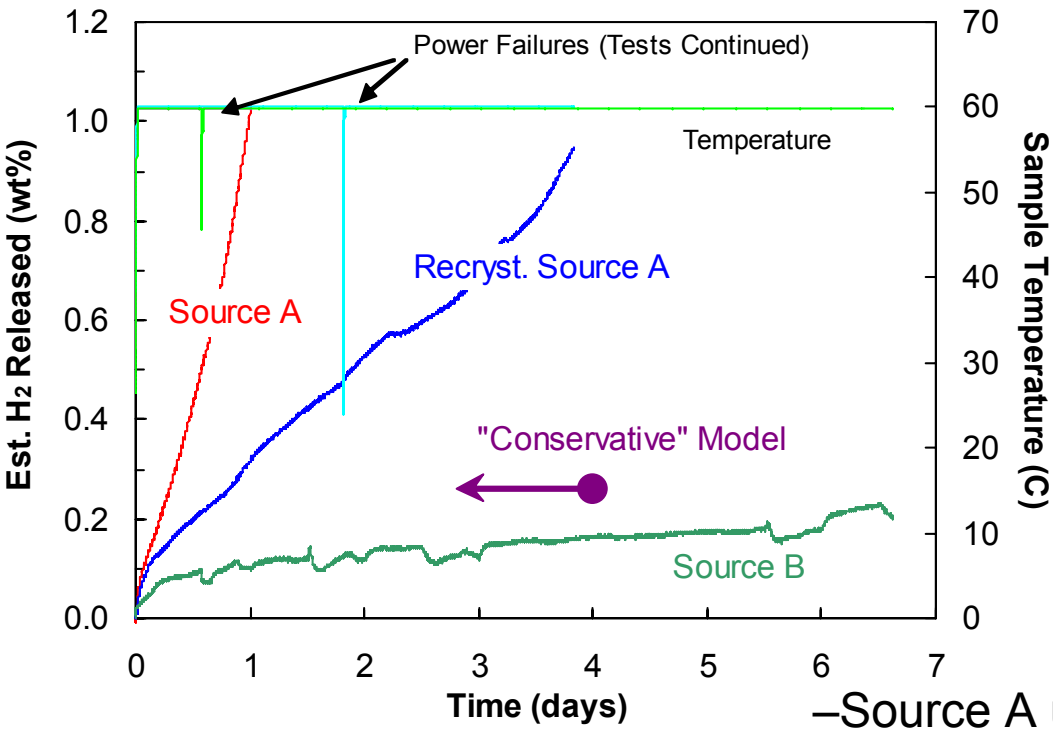
- Mechanism for the onset of release
  - Confirmed nucleation and growth mechanism
  - DADB intermediate is key to release
  - DADB, other additives increase rate
  - Mechanism valid up to ~ 120°C





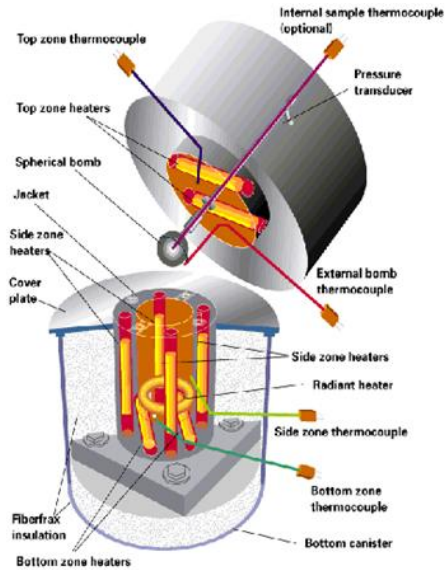


- Shown that AB is stable at 50/60°C and that impurities have a large impact on release

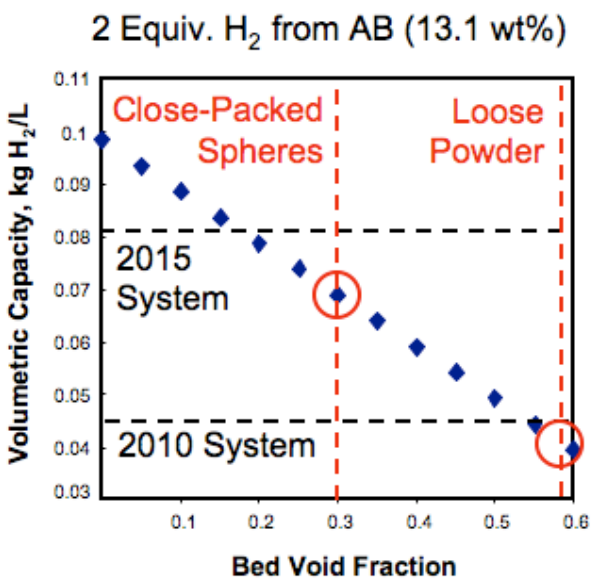


–Source A unstable
–Source B stable

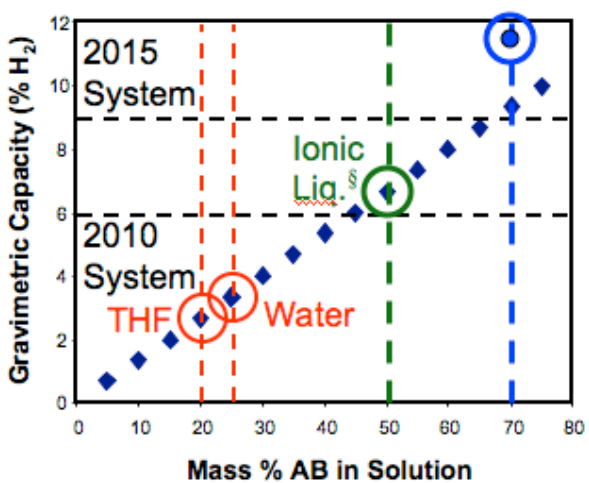
- Accelerated rate calorimeter



Engineering Assessments of AB as a Fuel

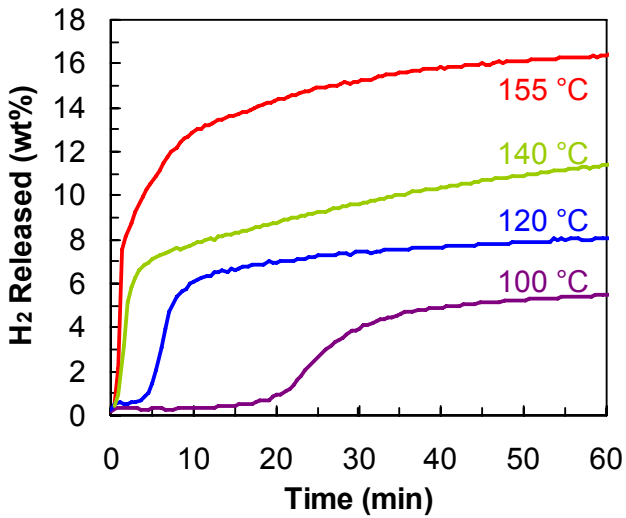


- To succeed with solid AB, much higher packing density is required
- Higher extent of release is required

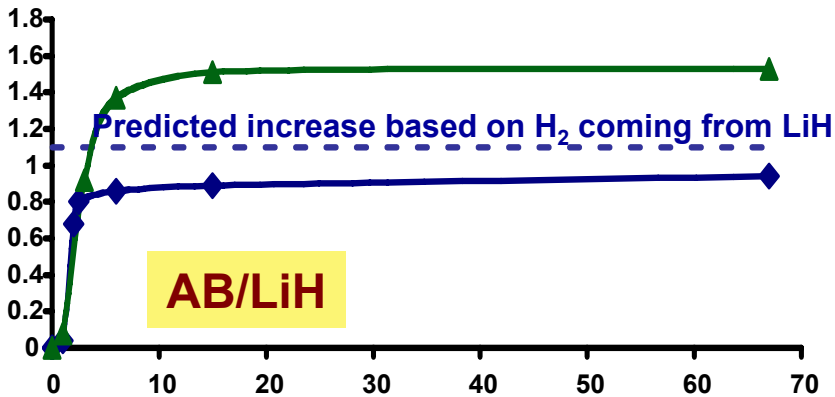


- To succeed, solvents that do not contribute to hydrogen release will not make the 2015 target.
- Need greater extent of release and at higher rates
- Need liquid formulations of fuel

- High Temperature enhances rate and extent of hydrogen release from solid AB
  - Wt% > 16% H_2
  - Max rate > 3 gH_2/s/kg AB
  - Virtually no induction period observed at higher temperatures

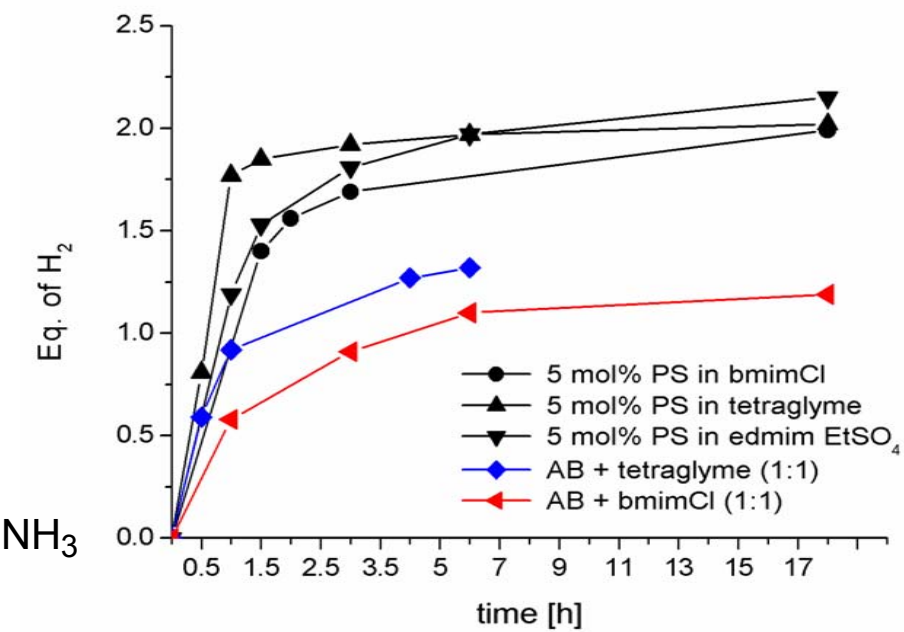


- Additives – enhance release and maintain stability



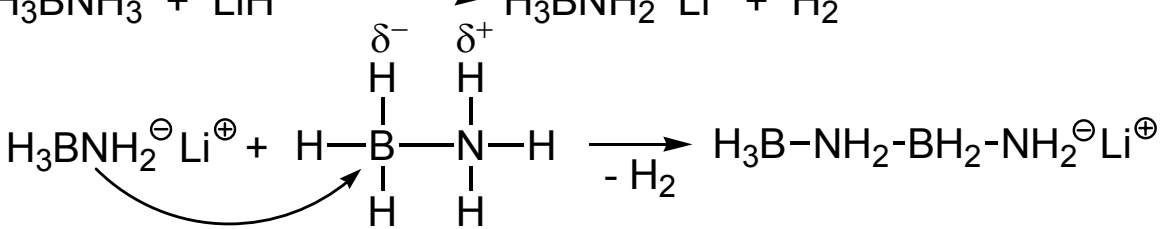
Hydrogen Release from AB in Ionic Liquids

- AB/Ionic liquids - no induction period
- Anionic polymerization mechanism with $LiNH_2$ or LiH additives



$$H_3BNH_3 + Li^{\oplus}NH_2^{\ominus} \longrightarrow H_3BNH_2^{\ominus}Li^{\oplus} + NH_3$$

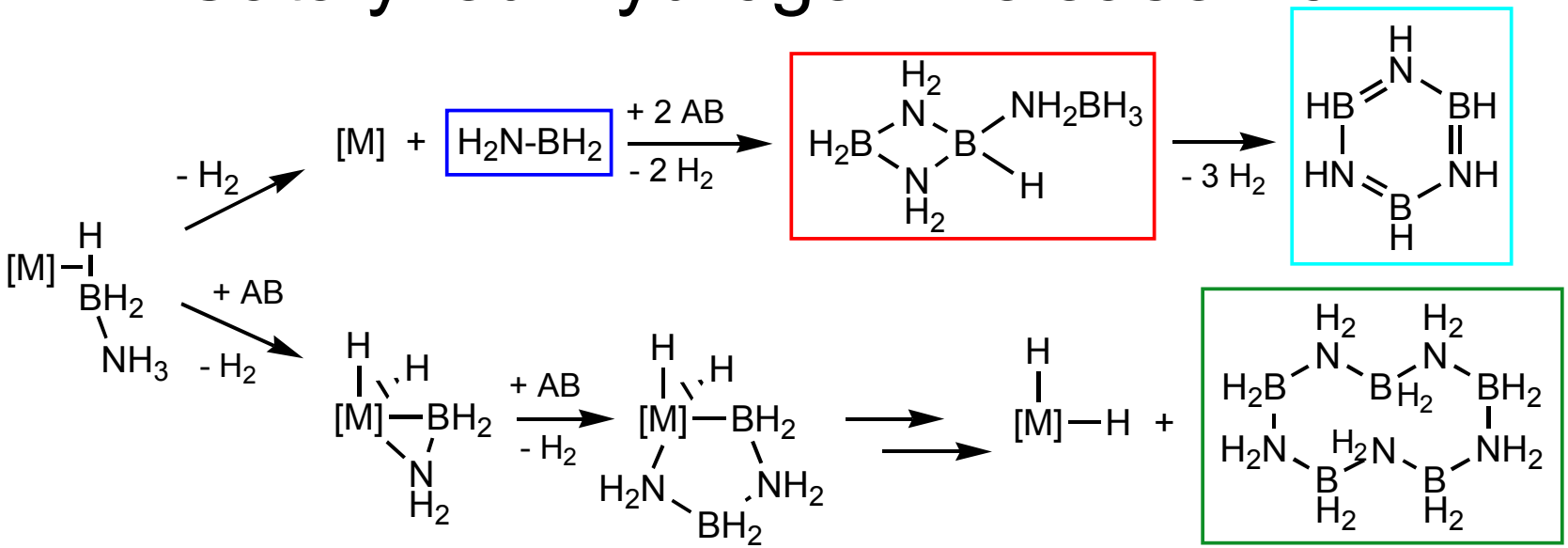
$$H_3BNH_3 + LiH \longrightarrow H_3BNH_2^{\ominus}Li^{\oplus} + H_2$$

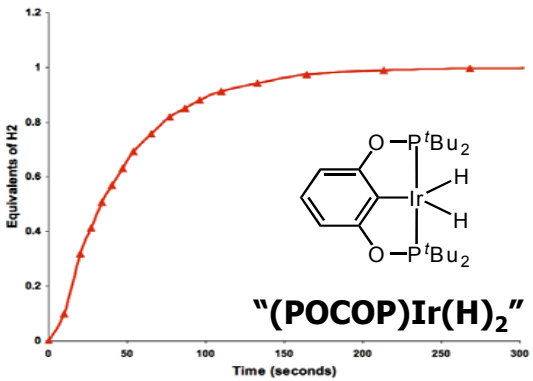


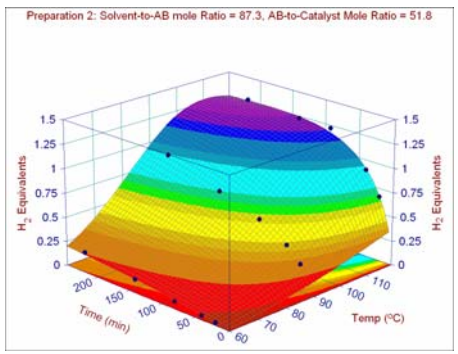
$$H_3B-NH_2-BH_2-NH_2^{\ominus}Li^{\oplus} + H_3BNH_3 \xrightarrow{-H_2} H_3B-NH_2-BH_2-NH_2-BH_2-NH_2^{\ominus}Li^{\oplus}$$

Computational studies of this mechanism are underway at Alabama (Dixon)

Catalyzed Hydrogen Release from AB



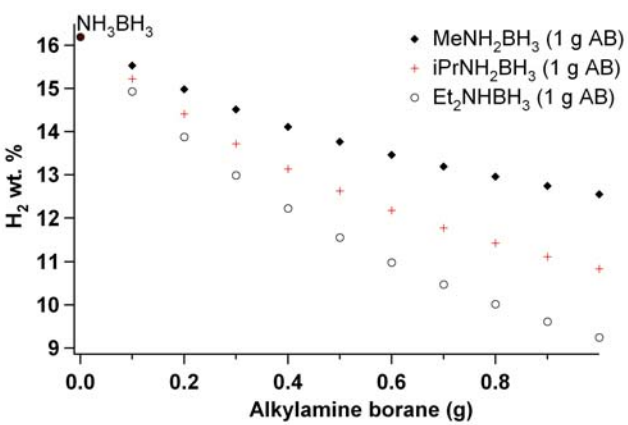




- Mechanism of H_2 release from AB may proceed via multiple pathways that impact the rates and extent of release
  - Ir releases only 1 equivalent via the cyclic pentamer
  - NiNHC catalysts release 2 equivalents via borazine

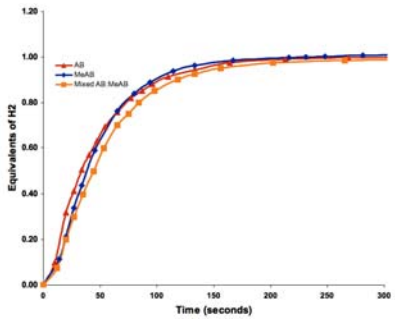
Catalysis of Mixed MeAB/AB Liquids

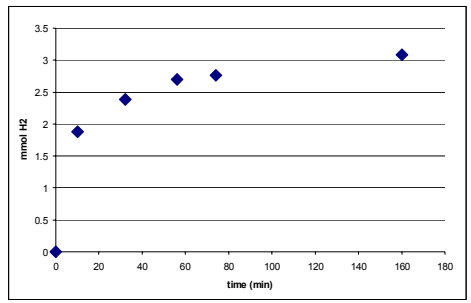
- Engineering assessments indicate that AB in non-hydrogen releasing solvents will not achieve the 2015 targets.
- Mixtures of amine boranes with ammonia borane contain varying weight percentages of H_2
- MeAB/AB mixtures contain quantities of H_2 that may achieve 2015 targets



- NAU has found low melting mixtures of AB with MeAB that are being examined as potential liquid fuels

- U. Washington's Ir catalyst (left panel)dehydrogenates MeAB and MeAB/AB mixtures at the same rate as pure AB
- An important observation -- products of mixed AB dehydrogenation are liquids as well.





- A LANL catalyst dehydrogenates MeAB/AB mixtures to release nearly 2 equivalents of H_2 (right panel)

Key Results: Hydrogen Release from Amine Boranes

- 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. % H_2
  - Fuel stability studies ongoing
- Metal Catalysis
  - Improved mechanistic understanding drives catalyst design
  - Equally rapid release of 1 H_2 from AB and MeAB with Ir catalysts at room temperature
  - Greater extent of H_2 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 (-1H_2) results in soluble spent fuel products

Materials Comparisons and Progress: Selected Results

Metrics	Hydrolysis			Thermolysis/Chemical Promoters				
	Penn AT (1.1 mol % Rh)	MCEL 30 wt% aq. SBH	Missouri $K_2B_{10}H_{10}$ Rh	PNNL AB solid 120 °C 140 °C	PNNL AB solid 155 °C (avg. rate to n H_2)	Penn AB/$LiNH_2$, 85 °C, 3 hr	Penn AB/AT/PS, solid state 85 °C, 3 hr	Penn AB/AT/PS, ionic liquid, 85 °C, 3 hr
Grav. density (Mat. wt%)	6.1, 4h	Material 7.3% System 4.5%	5.6	7 >13	>16	5.9	6.9	6.5
Vol. density (kg-H_2/L	0.090, 4h	System .037	.083	.021 .039	.048	.047	0.059	0.060
H_2 Flow Rate (g/s) per kg	0.0042, 4h	System 0.024	-	1 (max rate) 1.8 (max)	.84 (1 H_2) .22 (2^+ H_2)	.0055	0.0064	.0060
Kg of Mat. for 0.8 mol/s	377, 4h (halted work)	-	1.8	2 (max) 1 (max rate)	0.8 (max rate)	295	250	267

DOE System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)

4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

Volumetric Density (Kg-H_2/L)

0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

Materials Comparisons and Progress: Selected Results

Metrics	Catalysis						
	UW Ir, AB w/solvent, 23 °C	LANL Ni, MeAB/AB (neat) 80 °C	1: 1 MeAB/AB Theoretical, 2 equivalents H_2	LANL Ni cat 2% AB, in solvent 80 °C	Extrapolated Ni AB, saturated sol'n	LANL Ru cat, 2% AB in solvent 80 °C	LANL Bronsted Acid; 20 wt % AB, 60 °C 18 hr
Grav. density (Mat. wt%)	0.4 (4.9 - no solvent)	5.7	11	.015 10.8 - no solvent	1.8	0.019 13.5 - ns	1.7
Vol. density (Kg-H_2/L Mat.)	0.005	0.06	0.12	0.00015 .08 - ns	.03	.00019 .1 - ns	0.016
H_2 Flow Rate (g/s) per kg Mat.	0.068 0.82 - ns	0.02	-	0.00002 .016 - ns	.004	0.0001 .01 - ns	18 hrs -- too slow
Kg of Mat. for 0.8 mol/s	24 2 - ns	100	-	70,000 98 - ns	400	16,000 160 - ns	work halted

[ns -- no solvent included in calculation]

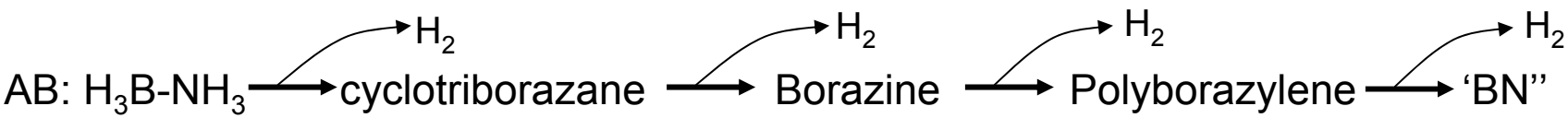
DOE System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

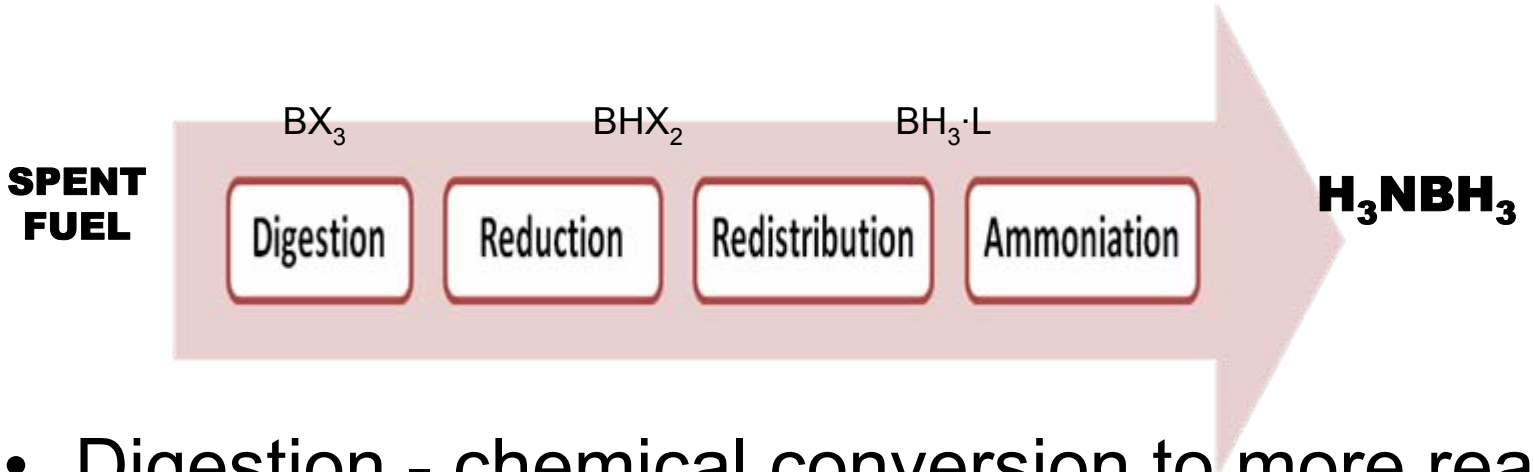
Volumetric Density (Kg-H_2/L)
0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

Regeneration of Spent AB

- Goals: Regenerate AB from spent fuel
  - Mixtures of ‘BNH_x’: borazine (x=1), and various forms of cross-linked polyborazylene (x<1)



  - ‘Digest’ and rehydrogenate BNH_x back to ammonia borane via processes that are > 60% efficient



- Digestion - chemical conversion to more readily processed BX_3 compounds
  - This step may 'lose' residual B-H in the spent fuel
- Reduction - conversion of B-X bonds into B-H bonds
- Redistribution - conversion of $LBHX_2$ into LBH_2X and BX_3; and LBH_2X into LBH_3 and BX_3
- Ammoniation - conversion of LBH_3 with ammonia into NH_3BH_3, AB

- Regeneration chemistry offers routes to tune efficiency:

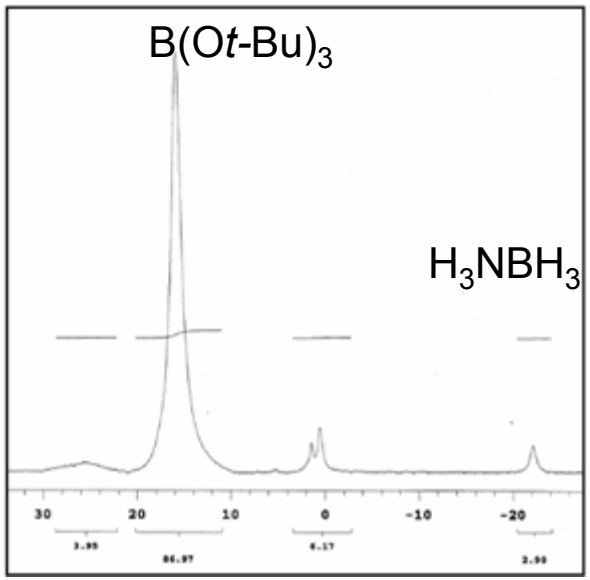
1) Digestion: $BNH_x + 3\ HX \longrightarrow BX_3 + NH_3 + H_2$
2) Reduction: $BX_3 + 3\ MH + NH_3 \longrightarrow H_3BNH_3 + 3\ MX$
3) MH Recycle: $MX + H_2 \longrightarrow MH + HX$

- May need to capture residual B-H from spent fuel

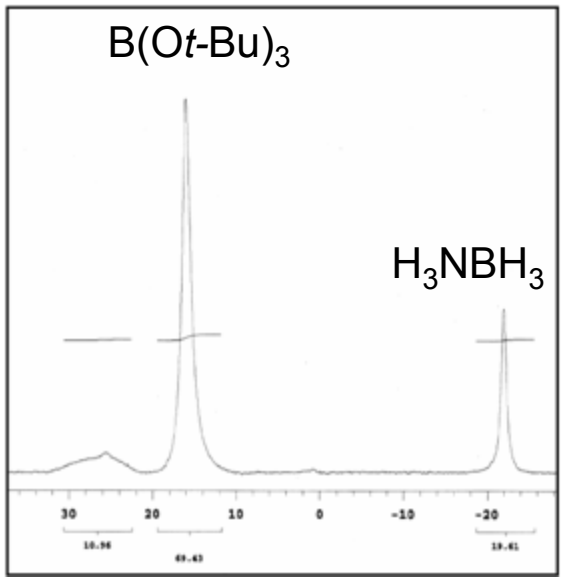
1) B-H Capture: $BNH_x + L \longrightarrow BNL_y + H_3BL$
2) Digestion: $BNL_y + 3\ HX \longrightarrow BX_3 + NH_3 + L$
3) Reduction: $BX_3 + MH + NH_3 \longrightarrow H_3BNH_3 + MX$
4) MH Recycle: $MX + H_2 \longrightarrow MH + HX$

- B-H capture has been demonstrated by using different alcohols in the presence of added ammonia:

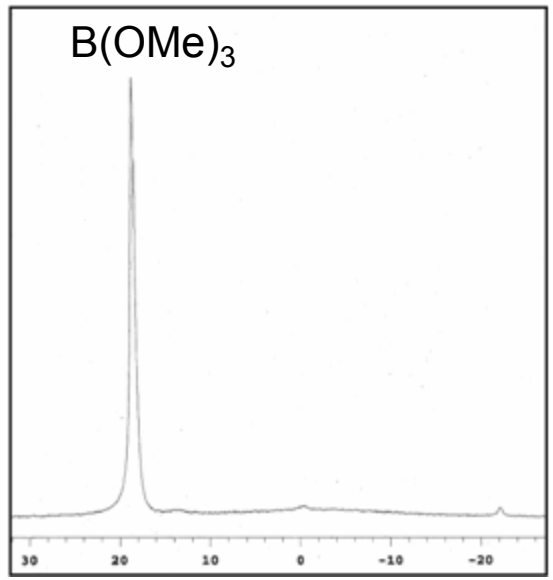
3 equiv. *t*-BuOH
36 h.



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



3 equiv. MeOH
211 psi NH_3, 12 h.



- MeOH favors loss of B-H to H_2 even in presence of ammonia
- T-Butanol favors retention of B-H bonds that may be converted back into AB

- Survey of a range of digestion agents results in a range of potential reducing agents that may be useful

- Energy efficiency of regeneration depends on the optimal selection of digestion agent, reducing agent, and conditions

Compound	**NaH/LAH**	**$HSiEt_3$**	**$HSnBu_3$**
BBr_3	Y	Y	Y
BCl_3	Y	Y	Y
$BHCl_2{\cdot}SMe_2$	Y	Y	Y
$BH_2Cl{\cdot}SMe_2$	Y	Y	Y
ClBCat	Y	--	Fast
Bu_2BOTf	Y	Y	Y
$B_3N_3Cl_3H_9$	Y	N	Y?
$BF_3{\cdot}OEt_2$	Y	Slow	Slow
$B(SPh)_3$	Y	Slow	Y
$B_2[(S\text{-}S\}Ar]_3$	--	--	Y?
HB[(NH-NH)Ar]	Y?	N	N
$B(OC_5F_5)_3$	Y	N	N
$(C_6F_4)OBCat$	--	N	N
HBCat	--	Slow	slow
B_2Cat_3	--	Slow	Slow
$B(OMe)_3$	Y	N	N

- Digestion of spent fuels using bromide demonstrated:

Digestion: $BNH_x + 4\,HX \xrightarrow{AlX_3} BX_3 + NH_4X$

X = Cl,Br

Coordination:

$$BX_3 + R_3N \longrightarrow R_3NBX_3$$

Reduction:

$$R_3NBX_3 + 3\,HMR_3 \longrightarrow R_3NBH_3 + 3\,XMR_3$$

M = Sn,Si

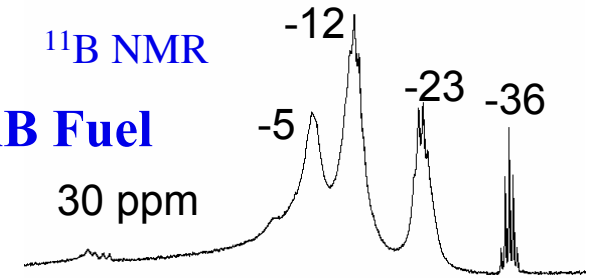
Ammoniation:

$$R_3NBH_3 + NH_3 \longrightarrow H_3NBH_3 + R_3N$$

Digestion of Spent Fuel mixture:

^{11}B NMR

Spent-AB Fuel

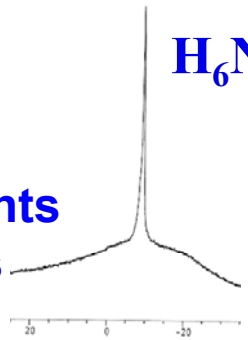


$\xrightarrow[CS_2]{HBr/AlBr_3}$

23 °C, 4 h

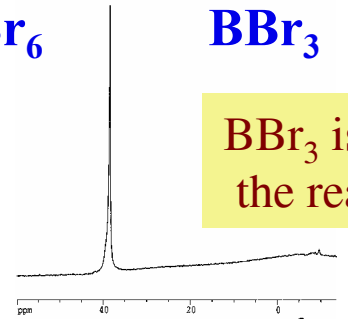
Product ratio depends upon spent-fuel reactants and conditions

$H_6N_3B_3Br_6$



+

BBr_3



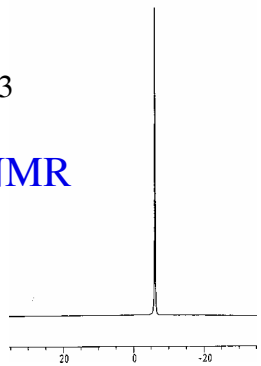
BBr_3 is distilled from the reaction mixture

Coordination and Reduction Accomplished in One Pot:

$$Et_3NBBr_3 + 3\ HSnBu_3 \longrightarrow Et_3NBH_3 + 3\ BrSnBu_3$$

Et_3NBBr_3

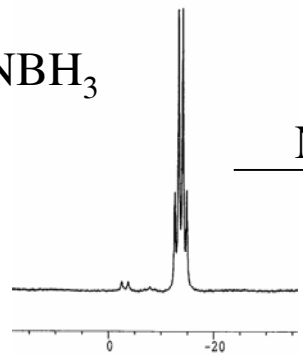
^{11}B NMR



$\xrightarrow{HSnBu_3}$

40 °C, 2 h

Et_3NBH_3

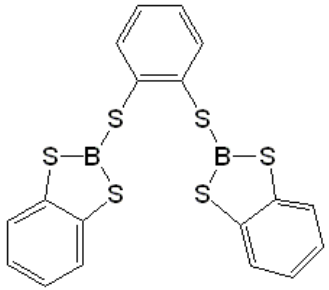


$\xrightarrow{NH_3}$ AB

• Digestion of spent fuel with thiols demonstrated

Digestion with thiols

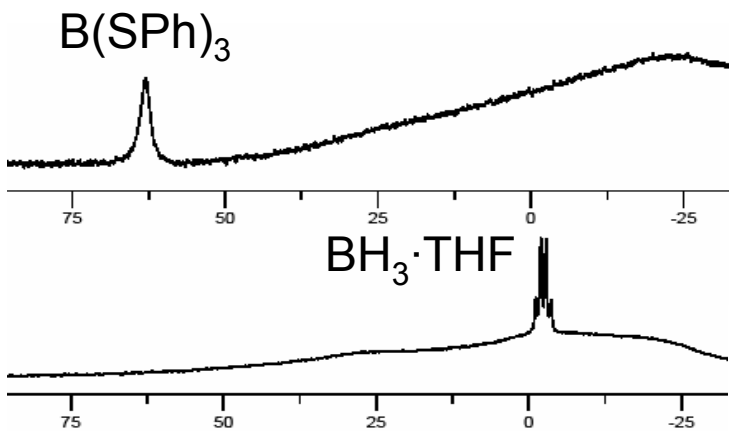
kcal/mol

		ΔH(298K)	ΔG(298K)
$2\ B_3N_3H_6 + 9\ [1,2\text{-}C_6H_4(SH)_2] \rightarrow 3$		$6\ NH_3 + 6\ H_2$	-5.9	-18.0

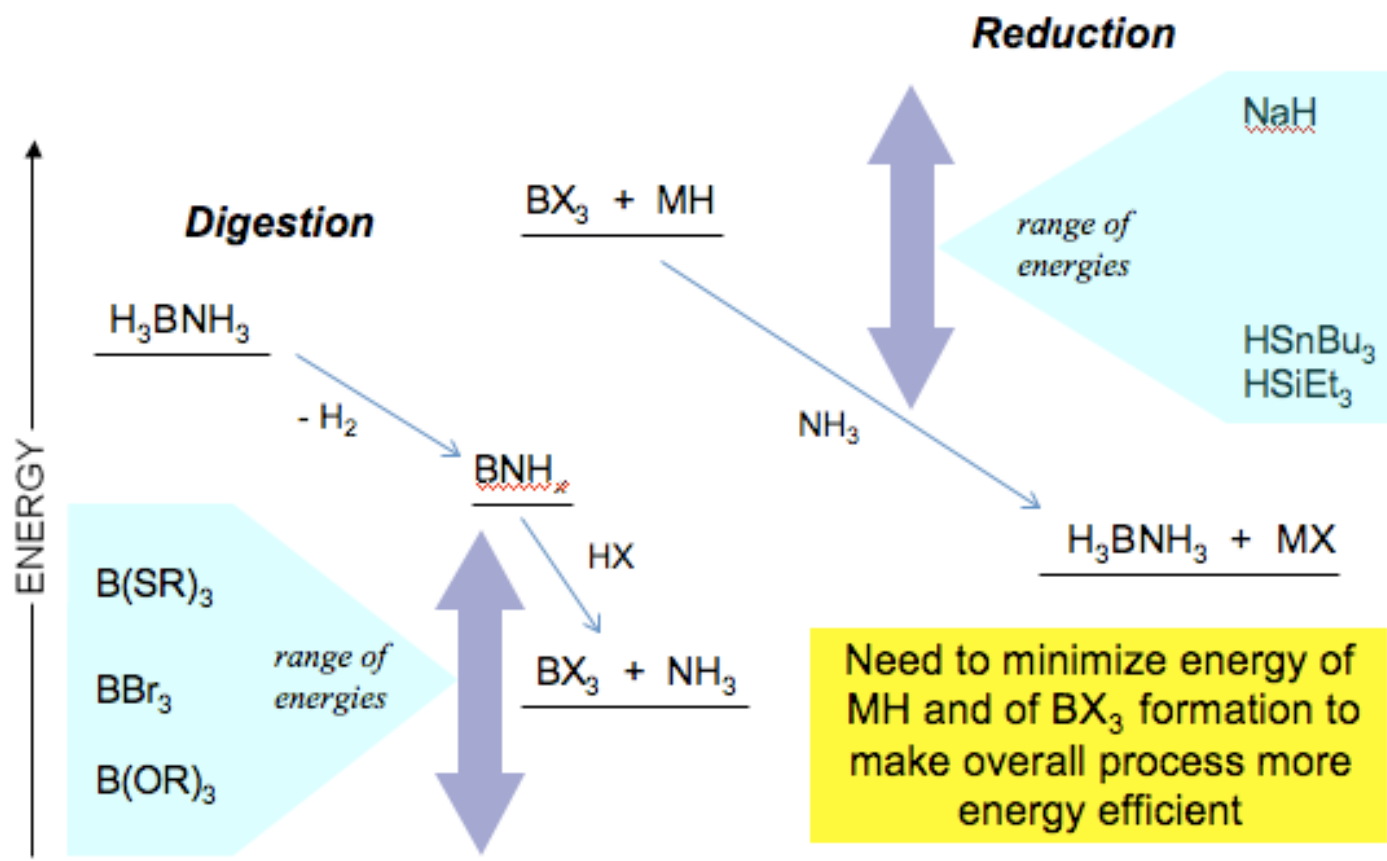
B3LYP/DGDZVP2

- Successful digestion using *o*-benzene-dithiol predicted using theory, and demonstrated experimentally
  - ✓ Reaction of borazine results in a mixture of HB(SCat), $B_2(SCat)_3$, and polyborazylene;
- Rapid reduction of B-S bonds in $B(SPh)_3$ has been achieved using tin hydrides

^{11}B NMR spectra



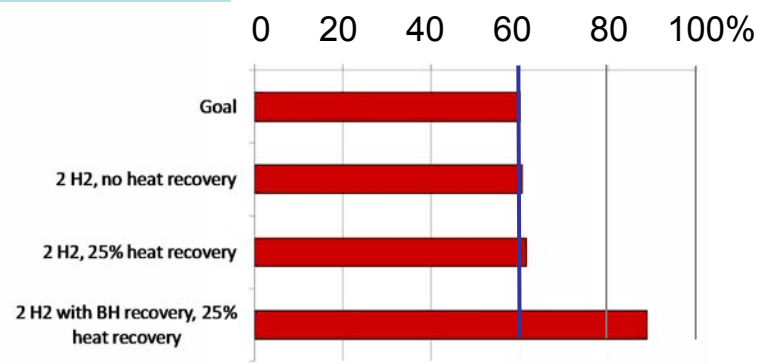
- Overall efficiency of regeneration process may be optimized by proper choice of digestion and reduction agents:



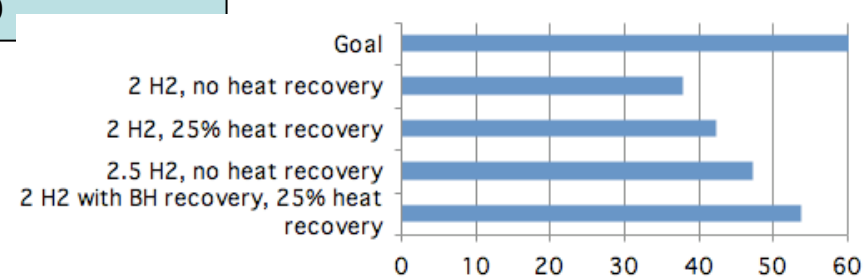
- Overall thermodynamic efficiencies of idealized processes has been calculated

$$\frac{(\text{Equiv. } H_2 \text{ stored})(57.8)}{(\text{Equiv. } H_2 \text{ used})(57.8) + \sum(\Delta H_{endo}) - (\%\text{ heat recovery})\sum(-\Delta H_{exo})} = efficiency$$

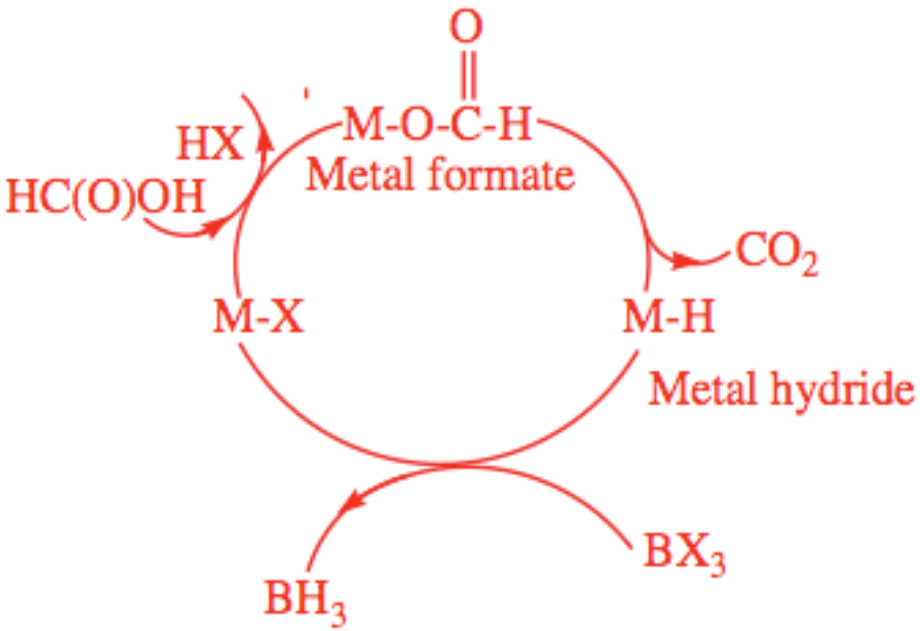
DIGESTION: 1/3 $B_3N_3H_6$ + 3/2 Ar(SH-SH) → 1/2 B_2[(S-S)Ar]$_3$ + NH_3 + H_2	10 kcal/mol
REDUCTION: 1/2 B_2[(S-S)Ar]$_3$ + 3 "HSn" + NH_3 → AB + 3/2 [Ar(S-S)]("Sn")$_2$	-14
MH RECYCLE: 3/2 [Ar(S-S)]("Sn")$_2$ + 3 H_2 → 3/2 Ar(SH-SH) + 3 "HSn"	8
DIRECT: 1/3 $B_3N_3H_6$ + 2 H_2 → H_3BNH_3	4



1)	⅓ $B_3N_3H_6$ + 4 HBr → NH_4Br + BBr_3 + H_2	-45.8 kcal/mole
2)	BBr_3 + 3 $HSnBu_3$ + NH_3 → H_3NBH_3 + 3 $BrSnBu_3$	-82.8
3)	NH_4Br → HBr + NH_3	45.1
4)	3 $BrSnBu_3$ + 3 H_2 → 3 HBr + 3 $HSnBu_3$	88.2
5)	⅓ $B_3N_3H_6$ + 2 H_2 → H_3NBH_3 (direct hydrogenation)	4.0



- Recycle of reducing agent a key step in overall regeneration process:
  - Center is exploring energy efficient routes to recycle of M-H from M-X through metal formate intermediates:



Future Regeneration
Catalytic Activation of H_2 for Reduction

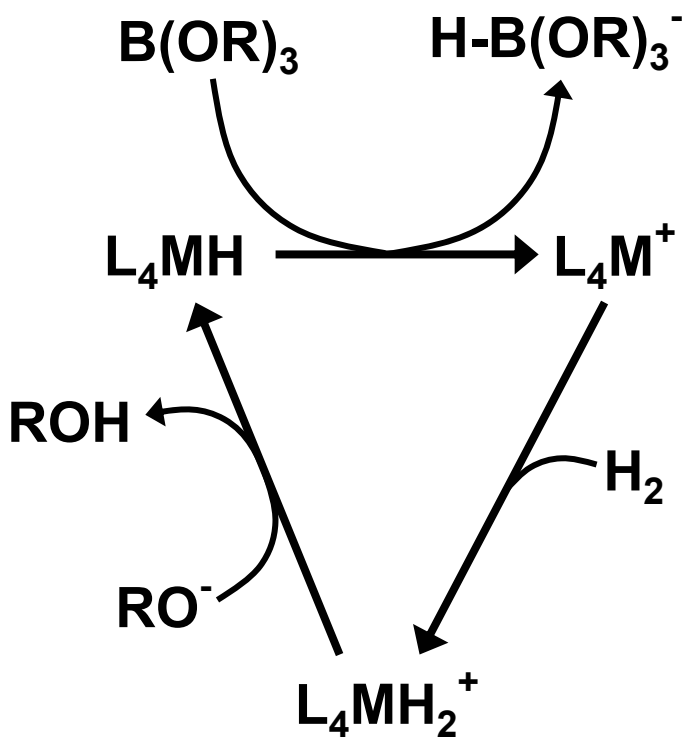
Dubois *et al. Organometallics* (2006)

$L_4M^+ + H_2 + t\text{-}BuO^- \rightarrow L_4M\text{-}H + t\text{-}BuOH$

$L_4M\text{-}H + BEt_3 \rightarrow L_4M^+ + H\text{-}BEt_3^-$

Theory: ΔG = -14 kcal/mol

$(PhO)_3B + H\text{-}BEt_3^- \rightarrow (PhO)_3B\text{-}H^- + BEt_3$



- Cannot reduce with H_2 alone
- Couple catalysis to acid-base chemistry to drive reaction
- Working on one pot reaction

Goal: $H_2 + Base + (RO)_3B \xrightarrow{Cat} (RO)_3BH^- + Base{\bullet}H^+$

Impact: route demonstrated by Dubois *et al.* should reduce $B(OPh)_3$

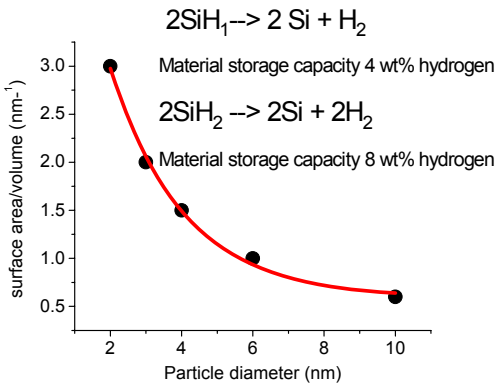
Key Results: Spent Fuel Regeneration

- *All steps of two potential regen chemistries demonstrated and efficiencies calculated*
- One demonstrated route has calculated thermodynamic efficiency > 60% (meets target)
- Routes to ‘save’ B-H in spent fuel via certain alcohols, thiols
- Energy efficient routes to M-X to M-H recycle being explored

Tier III: Advanced Concepts Poster Sub panel

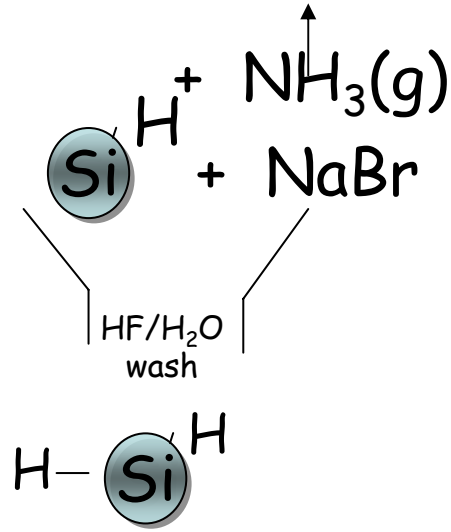
Nanomaterials

Goal: Design and test a high yield synthesis of light element main group nanoparticles with controlled size and surface chemistry to enable hydrogen release

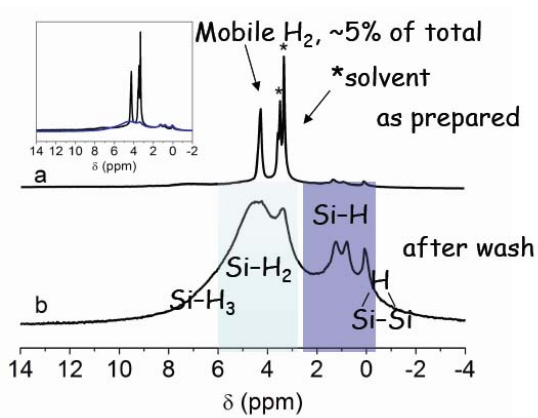


Synthesis:

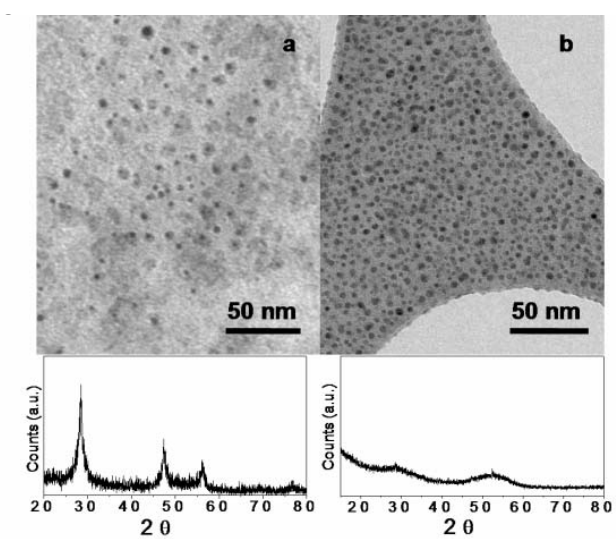
$NaSi + NH_4Br$ --->



Characterization:



H_2 release from 5 nm Si nanoparticle TG/MS showing ~3 wt % H_2 between 200-350˚C.

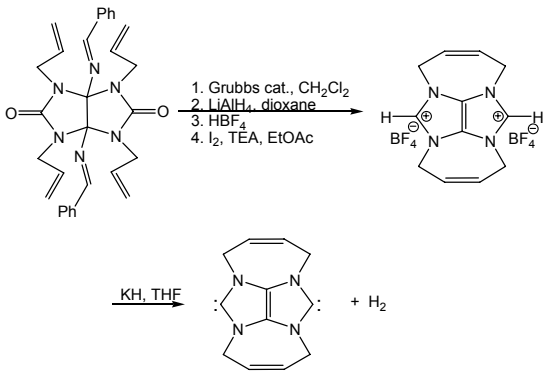


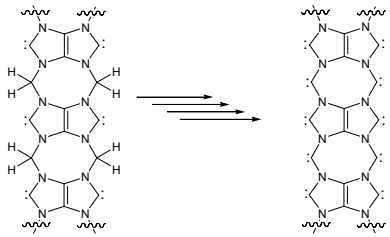
NMR shows that there is covalently bonded hydrogen on the surface. Some is present as SiH_2 which is important for mechanism of H_2 loss.

Organic materials

Heteroatom carbene systems designed to release H_2

Monomeric bis carbene synthesis

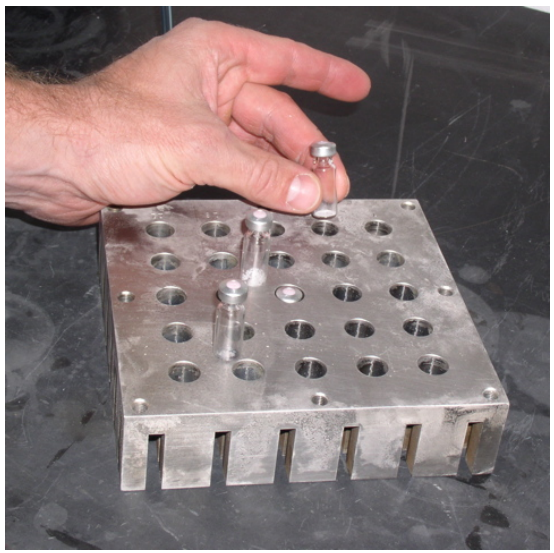




Polymeric bis carbene
Potentially stores 7.2 wt.% H_2

Rapid Throughput Experimentation

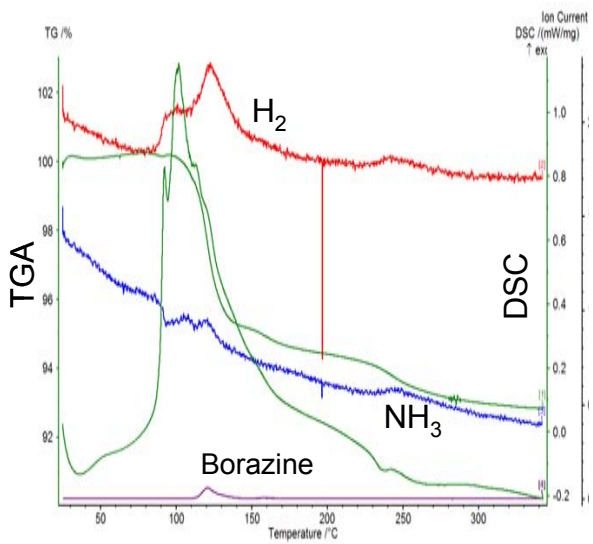
Large parameter spaces are required to be surveyed or optimized for both catalyzed H_2 release, and metal amine borane discovery research.



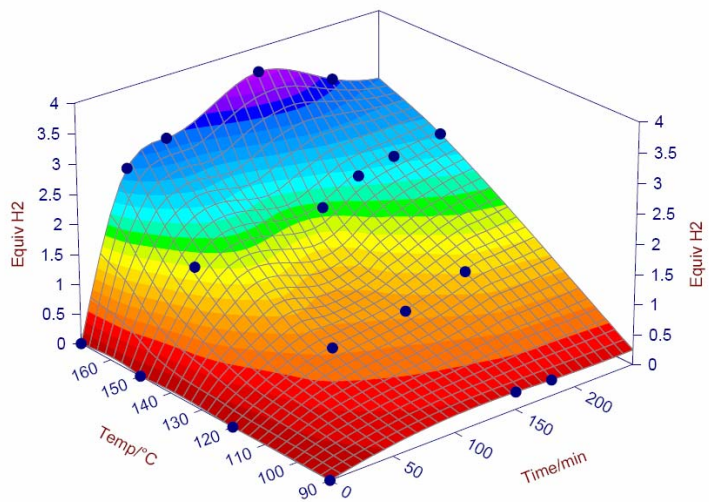
- Designed and fabricated two 25-well plate batch reactors
- H_2 quantification by gas chromatography
- Adding automated heating, shaking - future
- Automated headspace sampling - future

- Currently obtaining reaction data 25 at a time for
- H_2 release kinetics
- H_2 quantification versus composition

- International Partnership for the Hydrogen Economy (IPHE) - a new Center collaboration beginning Winter, '06
  - Metal amine boranes - potential up to 11.9 wt % H_2; reversible hydrogenation?
  - Staff exchanges:
    - IPHE partner to LANL and PNNL summer '07
    - LANL partner to Oxford, summer '07
- Early results appear promising, ability to 'tune' H_2 release



TGA - DSC - MS



7.2 % H_2 quantified by GC

Tier III: Materials Comparisons and Progress Selected Results

Metrics	Tier III Advanced Concepts				
	Organic Hydrides Theory	Coupled Reactions Theory	IPHE Theory	Nano Theory	Washington/ Alabama BNHC's Theory
Grav. density (Mat. wt%)	[0.9 -- 2006[a]] 2[b] 7.2	[4.4- 2006] -[c] 8-9	Measured 7.2 Max 10 - 11.9 Opt. 8-10.9	4.5[d] 8-11	- 7-8%
Vol. density (Kg-H_2/L Mat.)	['06-- .015]] 0.045	0.04	Measured 0.072	.1	tbd
H_2 Flow Rate (g/s) per kg Mat.	tbd	.008	Measured 0.02	tbd	tbd
Kg of Mat. for 0.8 mol/sec	tbd	195	Measured 80	tbd	tbd

a. benzimidizole, terminated; b. U. Alabama carbenes proposed;
c. 2007 work focused on IPHE, rapid screening; d. preliminary results on 4 nm particles

DOE System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

Volumetric Density (Kg-H_2/L)
0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

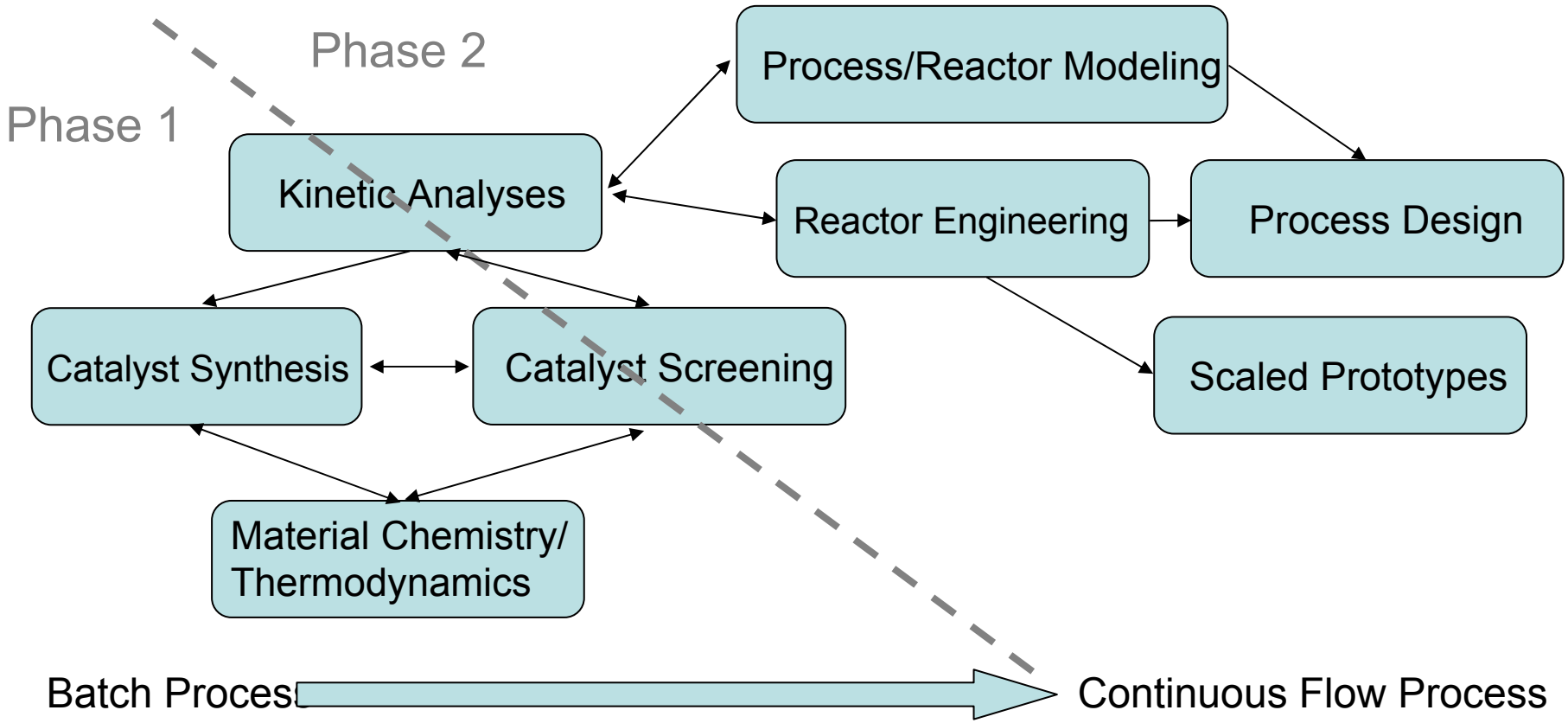
Crosscutting Poster Sub Panel

Engineering Assessment - General Overview of Activities

- Analysis of Sodium Borohydride Onboard release and offboard regeneration processes -- Rohm & Haas (lead), Millennium Cell, PNNL, LANL
- Fuel Stability and Safety: PNNL (lead), Rohm & Haas, NAU
- Hydrolysis Systems for SBH, others: Millennium Cell (lead), PNNL
- New Process Concepts for H_2 release, fuel/spent fuel transport, regeneration: PNNL, LANL, Rohm & Haas, Millennium Cell
- AB Regeneration -- assessment of efficiencies, process chemistry: LANL, Rohm & Haas, PNNL
- Catalysis -- assessment of requirements and needs for catalytic processes: LANL, PNNL

Engineering Approach

Developing the tools - modeling, experimental apparatus, and experiments - to move from batch processes to continuous flow processes as program transitions from Phase 1 to Phase 2



Theory and Modeling Crosscut Center Efforts for Early Assessment and to Guide Experiment

- Tier I Sodium Borohydride
  - Hydride reduction energetics (Rohm and Haas)
  - On-board reactor modeling (PNNL, MCEL)
- Tier II Alternative Boron Chemistries
  - Calculation of energetics of dehydrogenation reactions and reaction intermediates (Alabama, LANL, PNNL)
  - NMR chemical shift prediction in support of experiment (Penn, Alabama, LANL)
  - Thermochemistry of AB spent fuel regeneration: digestion, disproportionation, hydride transfer (Alabama, PNNL, LANL, Penn, UC Davis)
- Tier III Advanced Concepts
  - Calculation of Si-H vs. B-H bond energies to predict energetics of nanoparticle chemistries (Alabama, UC Davis)
  - Heats of formation and reaction enthalpies for heteroatom organics (Alabama, Washington)
  - Thermochemistry of IPHE project materials (Alabama, LANL, PNNL)

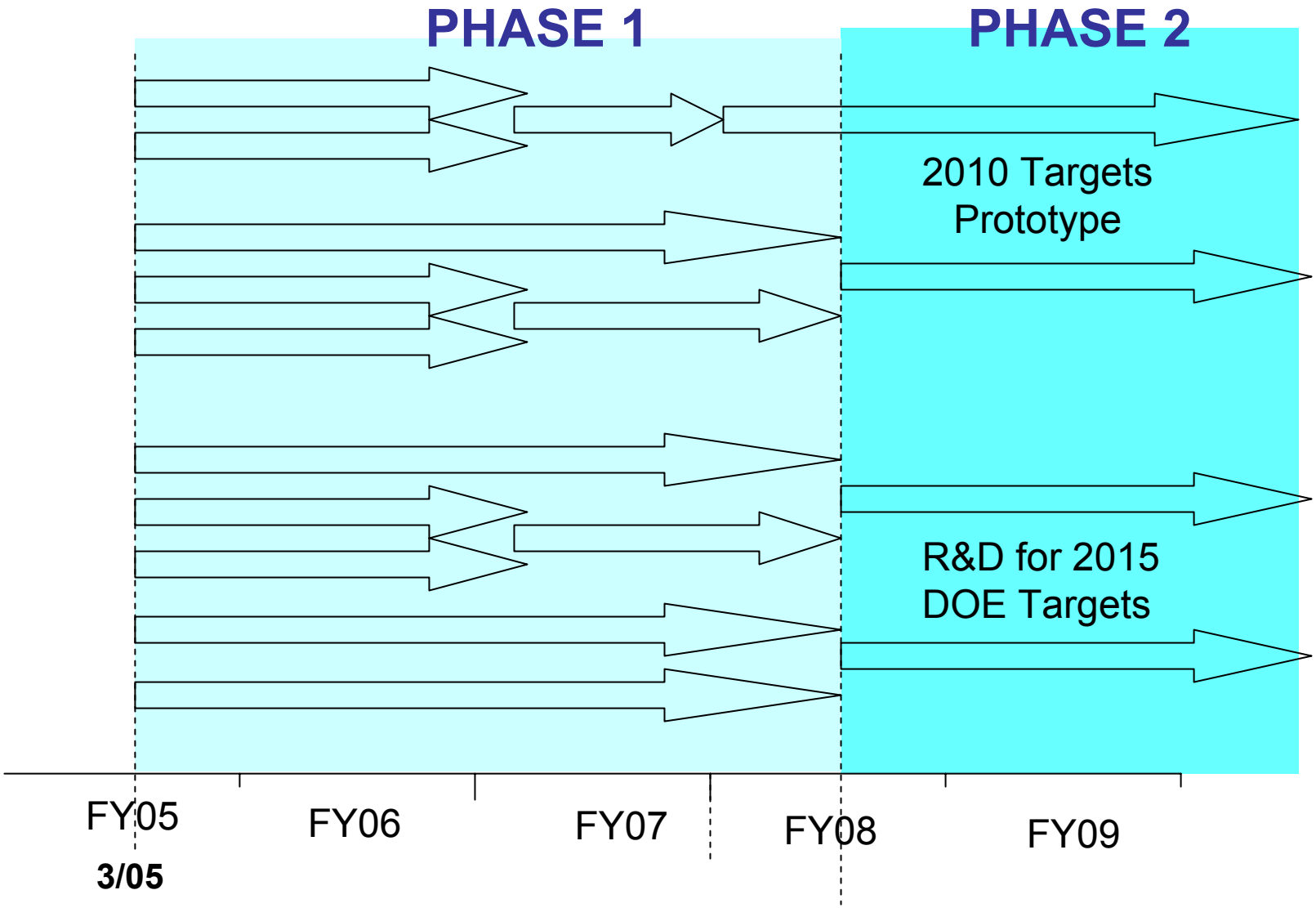
Looking Ahead

- SBH Go/No-Go decision
- Materials downselection process
  - Materials downselected for development to meet 2010 targets
  - Materials to move into the pipeline to meet 2015 targets
- Phase 2 partner workscope identification and selection

Future Research

- Continue to innovate and to develop many promising materials and regeneration options to maintain a ‘pipeline’ of candidates
  - High capacity materials with high rates of H_2 release
  - ≥ 2 H released / element; (AB = 2^+); more candidates needed
  - Innovate on release from organics ≥ 2H/C
  - Search for materials regenerable with H_2
  - Hybrid materials - e.g. IPHE project
- Improve efficiency of existing AB regeneration schemes
  - Novel digestion agents
  - Improved, efficient recycle of hydride transfer agents
  - Continue to search for liquid fuel compositions
  - Enhance rates, extent of release through catalyst design
- Continue to use quarterly reporting matrix to guide offramp decisions; re-direct resources where needed
- Engineering - move from batch to continuous processes

Phase 1 to Phase 2 Transition



Materials Down Select Process

DOE 2010 Target	Metric	Material 1	Material 2	Material n
System gravimetric Capacity (6 wt %)	g hydrogen released/g lab vessel	✓	✓	✓
System Volumetric Capacity (.045 kg/L)	kg hydrogen/L lab vessel	✓	?	✓
H_2 Flow rate (0.02 g/s/kW (80 kW stack)	ml lab reactor to achieve .8 mole H_2/sec	✓	✓	no
Regen Efficiency > 60 %	Based on LHV H_2, regen thermodynamics, demonstrated chemistry	✓	?	--
Auxiliary physical and chemical properties metrics	Solids, liquids, slurries, reactivity, handling, stability, byproducts, safety, etc.		?	

Materials down selections (current and to Phase 2) are based on progress (tracked quarterly) toward meeting DOE Targets

Phase 1 to 2 Down Selection Process : Partner Capabilities Mapped to Down Selected Materials

Partner Capabilities	Material 1	Material 2	Material n
Materials synthesis and characterization			
Catalysis and catalyst synthesis			
Kinetics and Mechanism			
Theory and Modeling			
Reaction engineering			
Process modeling			
Systems integration			
…			

Partners

Continued partner participation in Phase 2 will be determined within Center and based on capabilities required to achieve Phase 2 goals on down selected materials