Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Project ID# ST040

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2010 DOE Annual Merit Review

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start: FY 05
- End: FY 10
- 100% Complete

Barriers

- Weight and Volume
- Flow Rate
- Energy Efficiency
- Cost
- Regeneration Process
- System Life-Cycle Assessments

Budget

•FY 09

- $2,750 K

•FY 10

- $ 2, 000 K

Partners

- Chemical Hydrogen Storage Center of Excellence
- IPHE (UK, New Zealand)
- Hiroshima University, Japan

Relevance - Objectives

- Complete demonstration of regen process and provide data for preliminary cost analysis of NEW LANL regen process
- Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release
- Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation
- Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release (ΔG° = ideally no less negative than ca. –0.8 kcal/mol)
- Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream

Relevance - Milestones

	Make recommendations of materials, release and regen processes to DOE
	Catalog process details and result in DOE Storage Database
	Preparation to pass final report and associated information along to Engineering Center
	Finish analysis of hydrazine regeneration route
	Demonstrate details of 'one pot' regeneration
	Complete impurities quantification on most promising systems (solid AB, IL(s) AB)

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Approach: Los Alamos Technical Contributions

- Engineering Guided Research
  - Gas cell analysis of impurities in hydrogen release
  - Completed demonstration of regen process and provided data for preliminary cost analysis of NEW LANL regen process
  - Interfacing with Engineering CoE to transfer relevant materials data
- New hydrogen storage materials for portfolio
  - Design and synthesis of near-thermoneutral release materials
  - Design and synthesis of liquid fuel compositions
- Hydrogen Release
  - Identify reaction pathways to maximal storage and release rates
  - Design, synthesize, and demonstrate heterogeneous catalysts with high rates at T < 100 °C
  - New Base Metal catalysts

- Regeneration
  - Demonstrate all individual steps to ammonia borane from spent fuel and begin process integration
  - Refined stoichiometry, concentrations, separations, substitutions, reaction times, materials properties etc
  - Completed demonstration of regen process and provided data for preliminary cost analysis of NEW LANL regen process
  - Use theory to guide toward most energy efficient matching of regeneration reactions

- Patents
  - Published – 8
  - Pending – 8
  - Disclosures – 6

Technical Accomplishments since last review

- A complete **one pot** regen cycle has been proven with overall yield of spent fuel digestion through reduction steps exceeding 90%. This method works for multiple spent fuel forms including spent fuels from ionic liquids giving ammonia borane.
- Cost Analysis on NEW LANL regen process underway in collaboration with DOW. LANL is providing all of the experimental data and conditions.
- Liquid fuel compositions, based upon ionic liquids, have been DOWN SELECTED to continue. Development of new ionic liquid fuel compositions with greater than 10 wt% hydrogen
- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to > 9 wt % H_2
- Hydrogen purity analysis system has been assembled and is operating to identify and quantify impurities in H_2 stream
- Preliminary analysis of filter requirements begun in collaboration with engineering center of excellence. Data indicates we need to minimize borazine production.

Ammonia Borane 20 wt% H_2 But ……

3 Ammonia Borane (H_3N-BH_3) → Spent fuel ($B_3N_3H_4$) + 7H_2↑ ***$\Delta H \approx$ -7 kcal/mol***

- Good news in that temperature necessary for fast H_2 release can be obtained from heat of reaction

- Bad news in that extra cooling may be required

- Process is too exothermic to consider direct dehydrogenation (off board regeneration needed)

- Side reactions are known and accelerated by overheating (difficult to control in large volumes of solid)
  - -Impurities
    - * Can lead to loss of material as well as fuel cell poisons
  - -Different spent fuel forms possible
    - * Can complicate regeneration

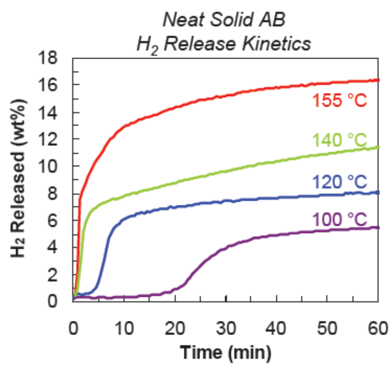
Solving the Issues: Kinetics in the laboratory

Solid release rates AMR 2007 St_28

Higher Temperature
Preliminary Data

DOE Hydrogen Program

- New gas burette apparatus allows release at higher temperature
- Working to higher temperature to further increase rate and capacity
- Wt% > 16% H_2
- Max rate > 3 gH_2/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

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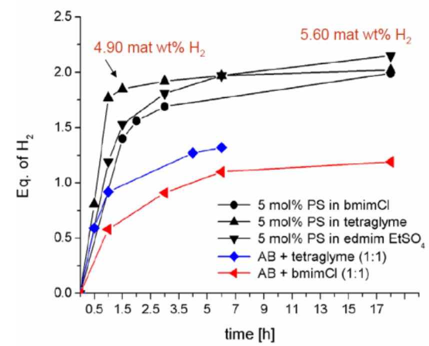
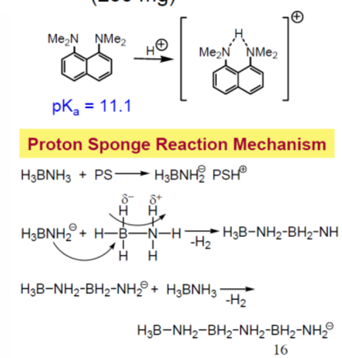
ILrelease rates AMR 2007 St_27

2007: Proton Sponge Increases H_2-Release from AB Solutions and Avoids the Formation of $M^+BH_4^-$ and NH_3

NH_3BH_3 + 5 mol % PS at 85 °C in Ionic-Liquids or Tetraglyme
(250 mg) (91 mg) (250 mg)





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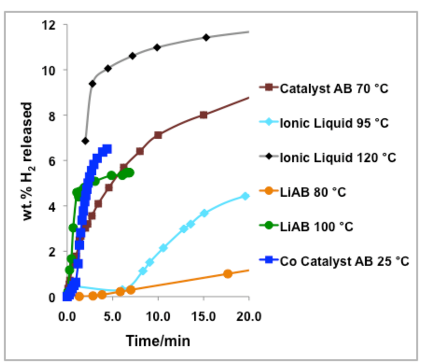
Catalytic release rates LANL 2009 St_17

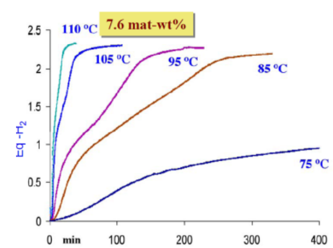


Thermal IL release rates AMR 2009 St_16

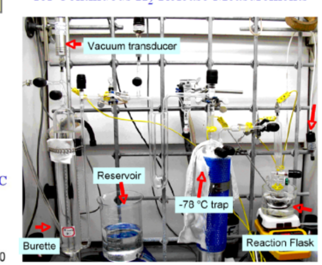
Technical Accomplishments

2009: Significantly Faster Rates for AB H_2-Release In Ionic Liquids with Only Small Temperature Increases

AB H_2-Release versus Temperature for 50 wt% bmimCl/AB



PNNL-Designed Automatic Gas-Burette Used for Continuous H_2-Release Measurements



Conclusion: Fast H_2-Release at higher temperatures, but need to increase mat-

Zheng et. al. *Rev. Sci. Instrum.* **2008**, *79, 084103*

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Hydrogen release kinetics are no longer a major issue

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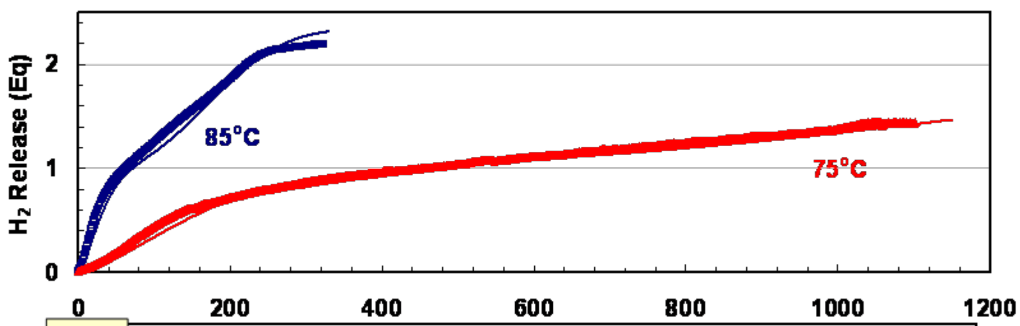
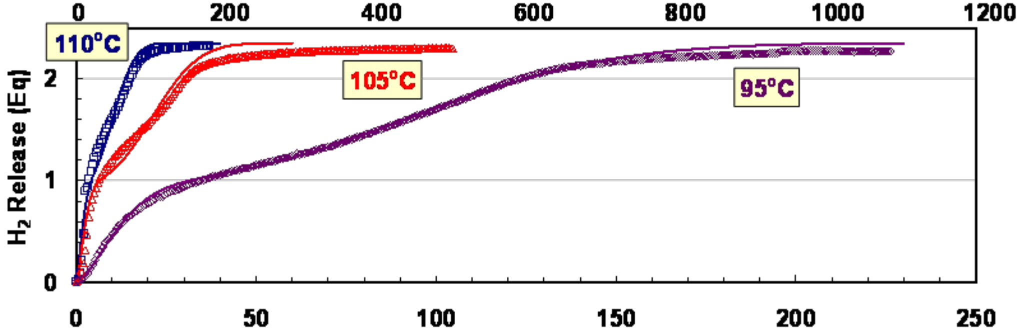
ANL analysis of ionic liquid release system

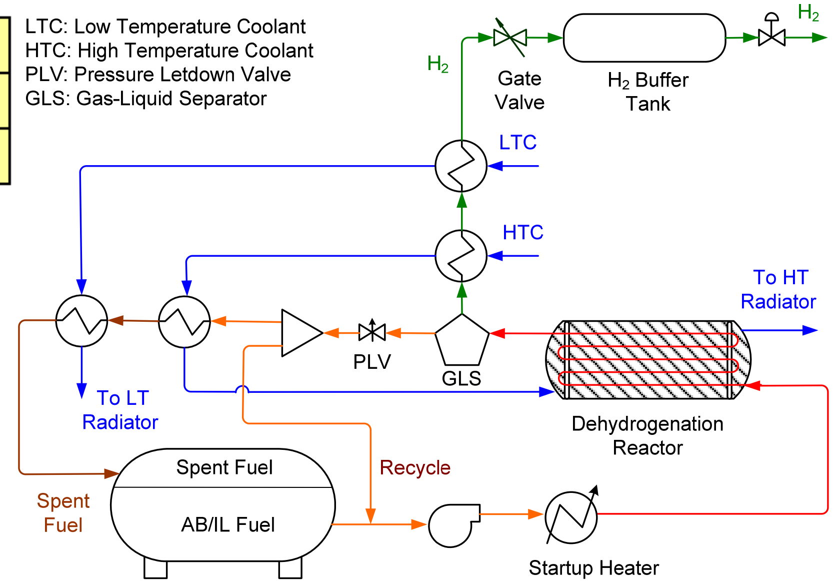
ANL kinetics model fits experimental thermal release data

$$d\alpha_i / dt = n_i k_i (1-\alpha_i)[-\ln(1-\alpha_i)]^{(n_i-1)/n_i}$$

	α	β	n	E (kJ/mol)
$R_1 \rightarrow R_2 + \beta_1 H_2$	$N_1/(N_1+N_2)$	1	1.5	142
$R_2 \rightarrow R_3 + \beta_2 H_2$	$N_2/(N_2+N_3)$	1.35	2.5	146







ANL dehydrogenation kinetics model and preliminary system analysis indicate that hydrogen release rates will meet the DOE target.
Heat rejection and startup/shutdown are key challenges

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Approach – Materials Development

Materials must meet CHSCoE 2007 down select criteria

2008-09 Discovery	2009 Analysis	2009-10 Go-NoGo

2008-09 Discovery

- Literature search
- Prescreen materials
  - H_2 Wt% must be in excess of 7%
  - Example $W(NH_2BH_3)_6$ = 8.3 wt%
- Materials synthesis

2009 Analysis

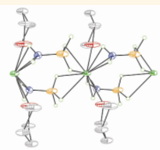
- Hydrogen release profile
- Characterization
- X-ray Structure
- Thermodynamics
- Impurities
- Feedback to discovery

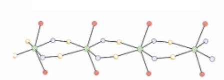
2009-10 Go-NoGo

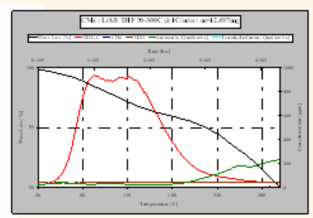
- Exothermic or endothermic?
- Improved release rates?
- Improved release volume?
- Fewer impurities?

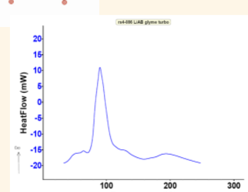
$MgCl_2 + 2NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)_2 + 2NaCl$
$MgCl_2 + NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)Cl + NaCl$
$ZnCl_2 + 2NaNH_2BH_3 \rightarrow Zn(NH_2BH_3)_2 + 2NaCl$
$TiCl_4 + 4NaNH_2BH_3 \rightarrow Ti(NH_2BH_3)_4 + 4NaCl$
$LiNH_2 + NH_3BH_3 \rightarrow LiNH_2BH_3 + NH_3$

AB derivative	H_2 wt%
$LiNH_2BH_3$	13.70 (2008)
$Ti(NH_2BH_3)_4$	12.05
$Mg(NH_2BH_3)_2$	12.00
$Sc(NH_2BH_3)_3$	11.24
$Li_2[Zn(NH_2BH_3)]_4$	10.15
$Ca(NH_2BH_3)_2$	10.10 (2008)
$NaNH_2BH_3$	9.54 (2008)
$LiZn(NH_2BH_3)_3$	9.34
$Zn(NH_2BH_3)_2$	8.06
KNH_2BH_3	7.31 (2009)
$Al(NH_2BH_3)_3$	12.97 (2009)







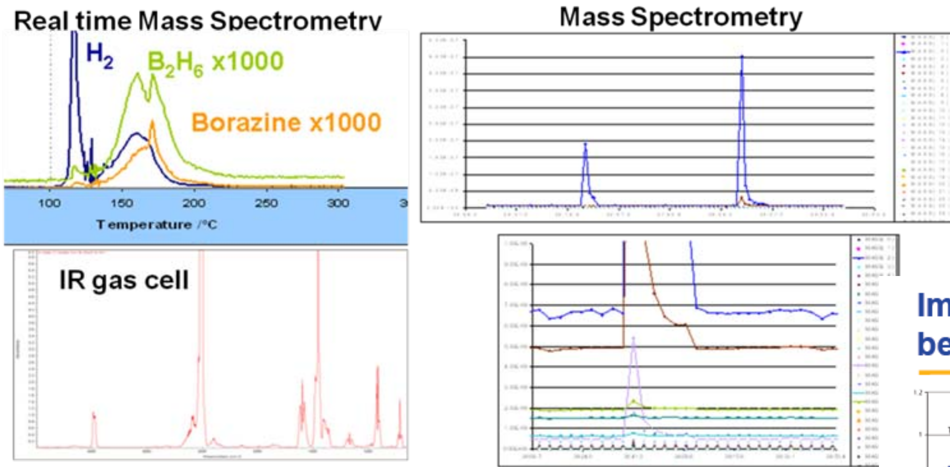


Compound	Normalized 1st exotherm J/g (onset/°C)	Normalized 2nd exotherm J/g (onset/°C)	Normalized 3rd exotherm J/g (onset/°C)	OnBoard
LiAB	-621.9 (77)*			No
KAB	+70 (71)	-48.6 (75)		No
Mg(AB)2	-6.7 (78)	-188 (108)		No
Ca(AB)2	-102 (101)	-56 (120)		No
Al(AB)3	-38.5 (66)	-5.1 (106)	-5.9 (150)	No

Impurities from solid AB AMR 2008 St_6

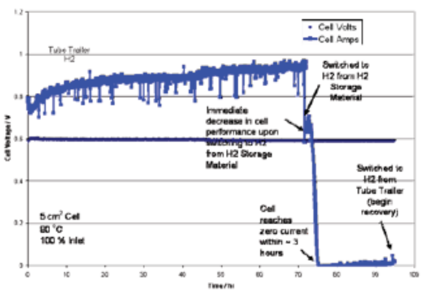
Hydrogen Stream Purity Capability is Enhanced

We have been looking at gas impurities for several years

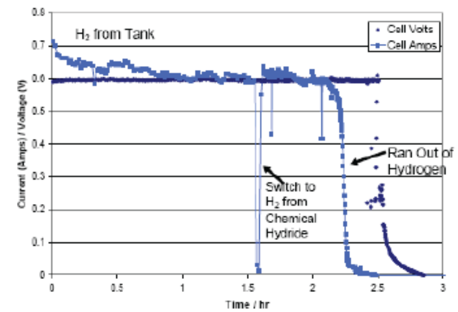


We can use spectroscopy and spectrometry for determining H_2 puri
But what about effects of very small, perhaps undetectable contaminants over long operating times?

Impacts from the H_2 Stream on Fuel Cell Operation can be determined



Raw H_2 from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst



Simple inline filter removes borazine, FC performance unaffected

Fuel cell recovered under clean hydrogen and analysis indicates catalysis was poisoned, not the membrane.

- Future Test hydrogen release systems H_2 purity using long term fuel cell operation

Collaboration with Rod Borup of the LANL Fuel Cell Durability Team

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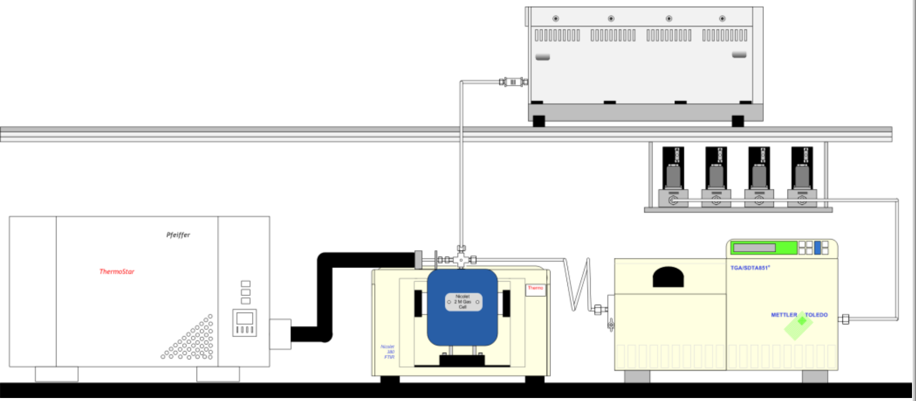
DOE Chemical Hydrogen Storage Center

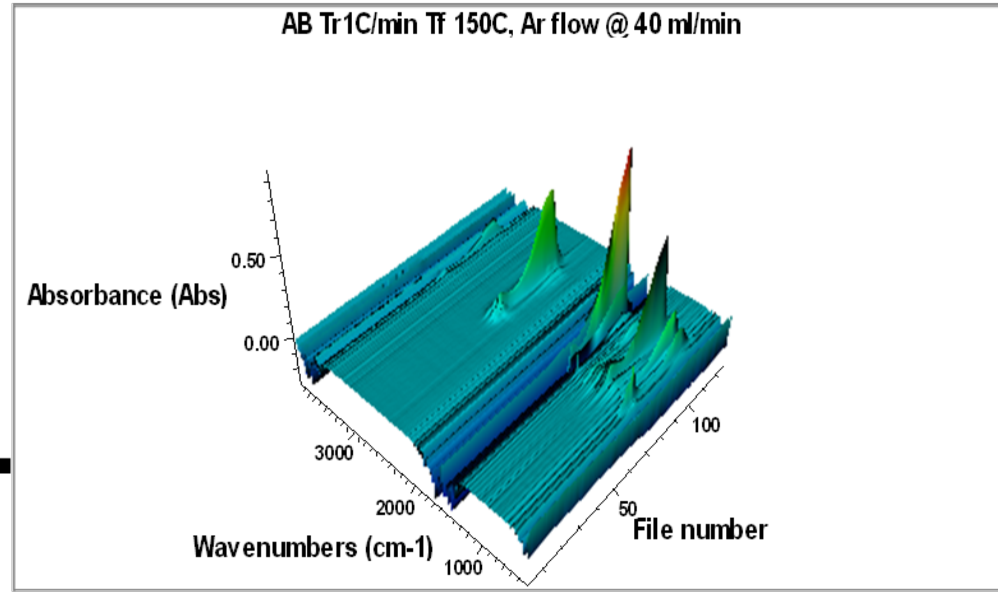
Slide 23

2010 Quantitative Gas Analysis of Thermal Release from AB

Impurities can be detected before major hydrogen release temperatures

	T_{onset}
Ammonia (963 cm^{-1})	~ 70 °C
Diborane (720 cm^{-1})	~ 86 °C
Borazine (2550 cm^{-1})	~ 86 °C





Pure solid ammonia borane produces large amounts of impurities.

Impurities and Mitigation (solid AB)

• Experimental Data

AB/MC Borazine Production

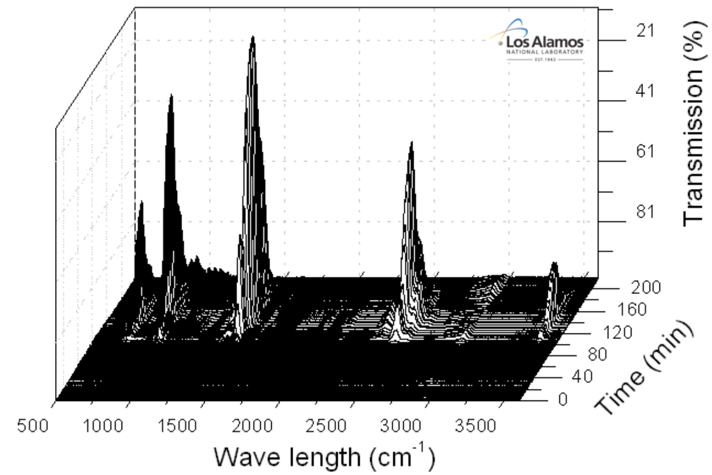
0.2 $mg_{Borazine}$/ $mg_{AB/MC}$ Reacted

Reaction Conditions: 30-200°C @ 5°C/min

Borazine Sorption Capacity

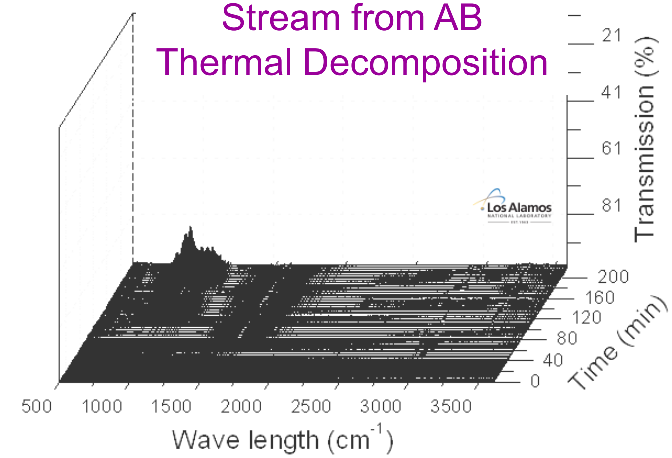
Activated Carbon (ACN-210-15):

0.26 $mg_{Borazine}$/ mg_{Carbon}



• Raw Product Stream from AB Thermal Decomposition

• Filtered Product Stream from AB Thermal Decomposition



• Carbon Sorbent Scaleup

- 5kg of H_2 results in 37kg of AB/MC (2.5 moles H_2/mole AB)

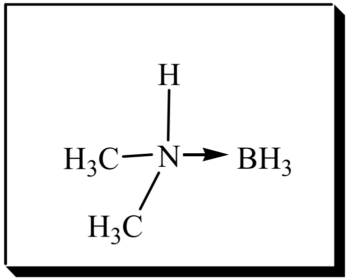
➡ 6.2 kg of borazine produced per fuel tank

➡ 24 kg of carbon per fuel tank

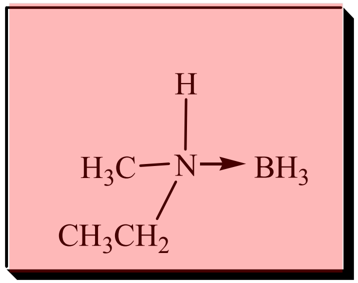
Center Approaches to hydrogen release: Faster rates, lower temps and cleaner hydrogen

- Additives to solid AB
- Solvents plus AB
- Homogeneous catalyst
- Ionic Liquids
- Heterogeneous catalyst
- Alkyl-AB / AB mixtures for liquids
- New cyclic derivatives
- Metal ammonia

2009 Liquid Fuels based upon alkylamine boranes

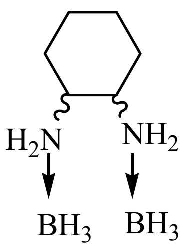


solid at RT, m.p. = 37°C

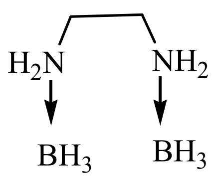


liquid at RT

liquid at RT

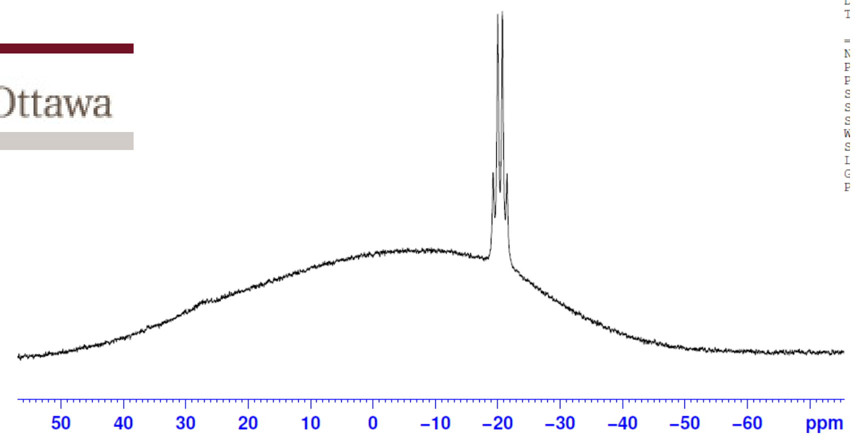


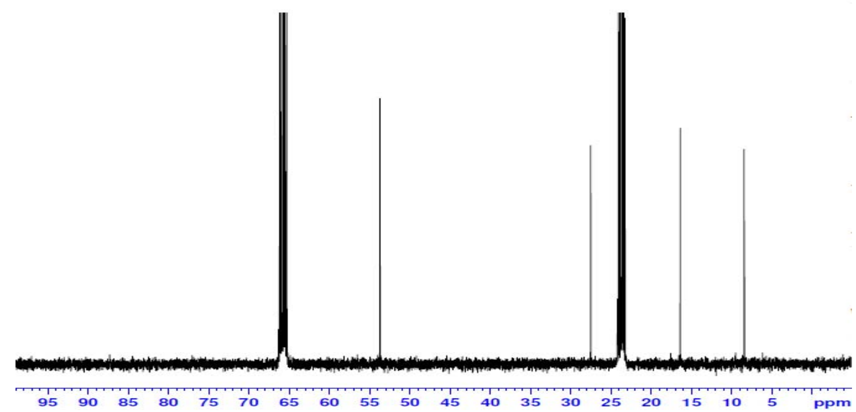
cis/trans cyclohexane-bisAB
pasty solid at RT



solid at RT

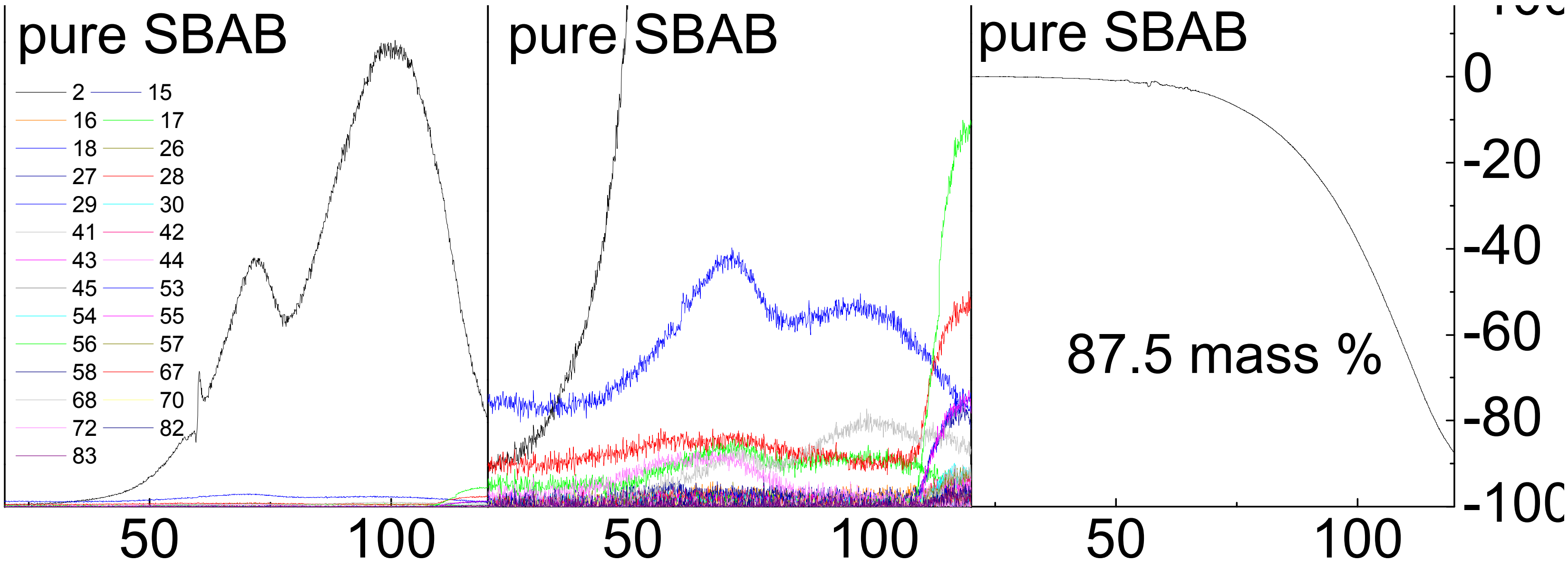
uOttawa



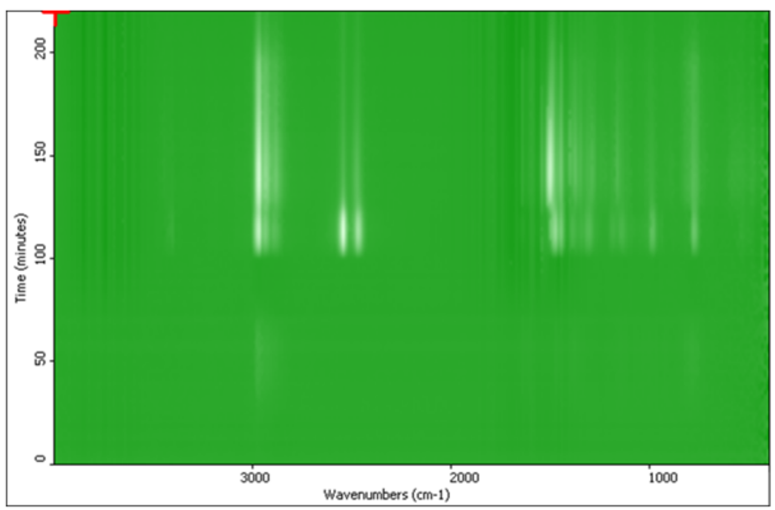


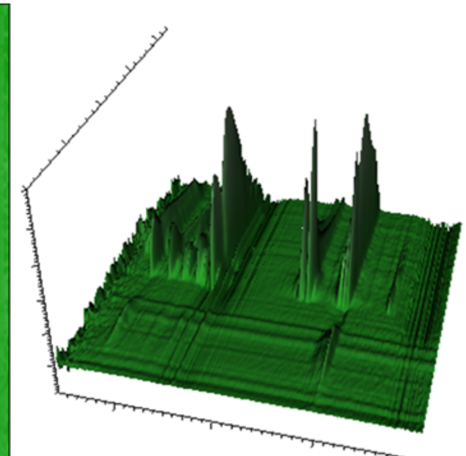
Last year sec-butylammine-BH_3 has shown the most promise with sec-butylammine-BH_3:AB 50:50 wt% mixtures liquid at below room temp.

2010 Alkyl-AB materials kinetics and impurities



Gas analysis of thermal profile of $secBuNH_2BH_3$ indicated significant impurities at temperature greater than 50 C





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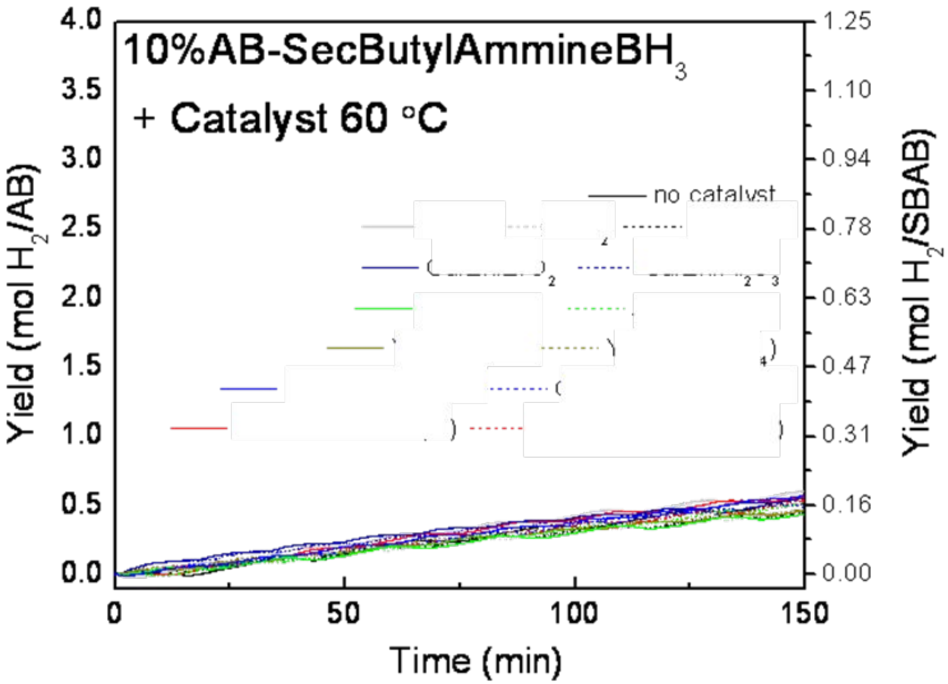
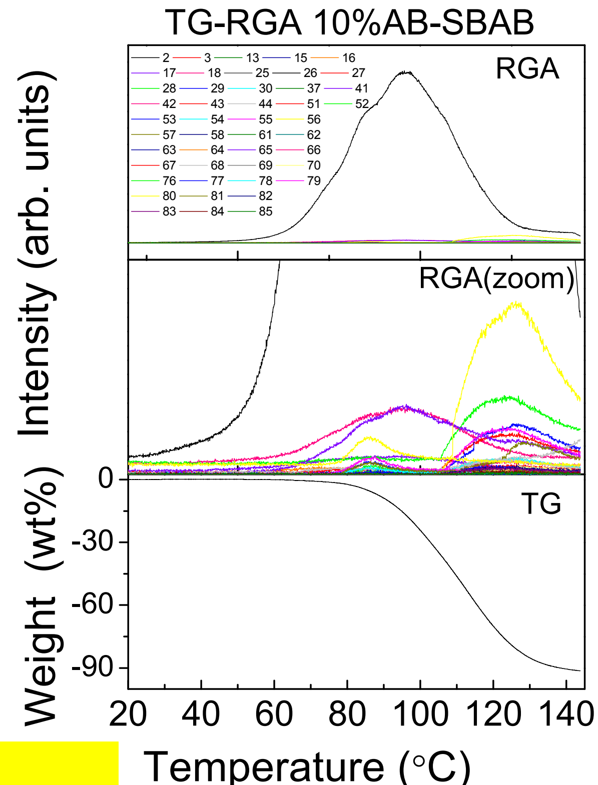
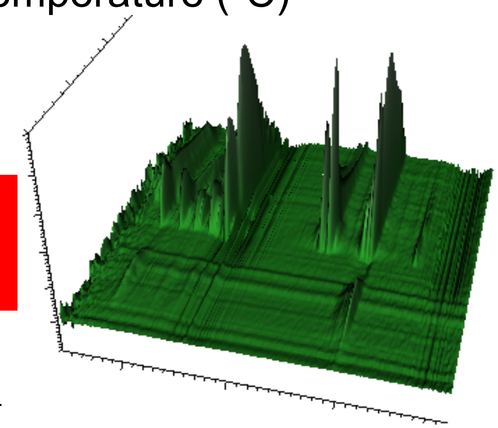
2010 Catalysts of Alkyl-AB – AB mixtures





No improvements were observed in the rates of hydrogen release possibly due to poisoning from Sec-butylNH_2. Gas phase impurities were significant.



<u>This approach to liquid storage systems has been halted at LANL.</u>

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Metal AB materials M-$(NH_2BH_3)_x$

Key: element name / atomic number / **symbol** / atomic weight (mean relative mass)

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

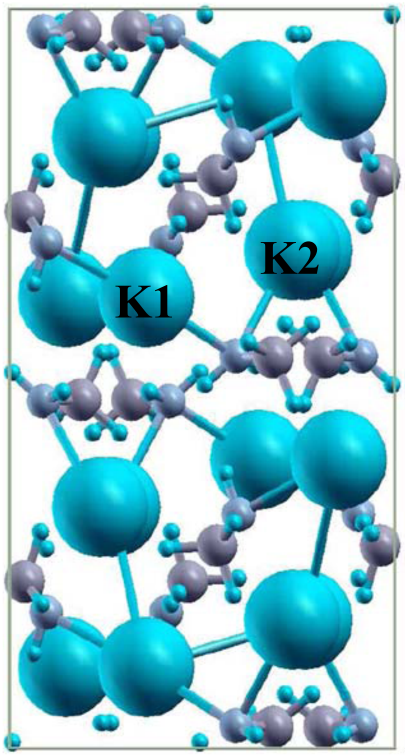
*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Metal-AB derivatives are now known for several metals.

KAB crystal structure

Y. Zhang and C. Wolverton, 2010

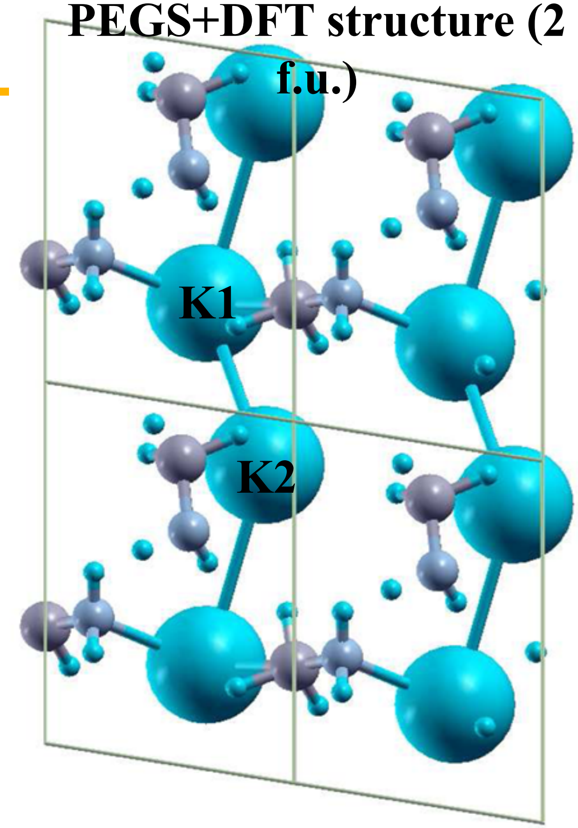
Experimental Structure (16 f.u.)



Space group: Pbca
a= 9.35 Å
b= 8.21 Å
c= 17.19 Å
α= 90.00
β= 90.00
γ= 90.00

Bond Lengths	Expt.	Theory (PEGS+ DFT)
K1-K2	4.26	4.24
K1-N	2.96	2.77
K1-B	3.38	3.08
K2-N	3.01	2.81
K2-B	3.12	3.02

Theoretically predicted PEGS+DFT structure (2 f.u.)

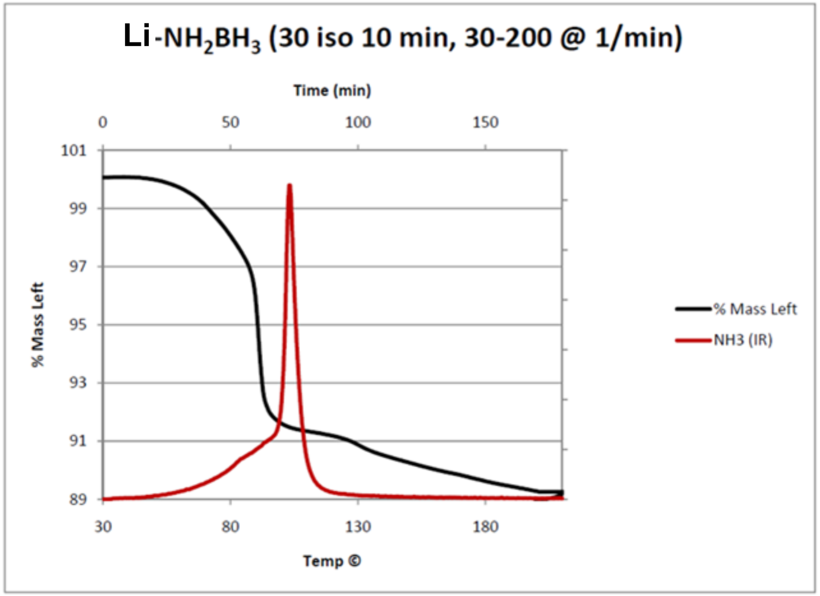


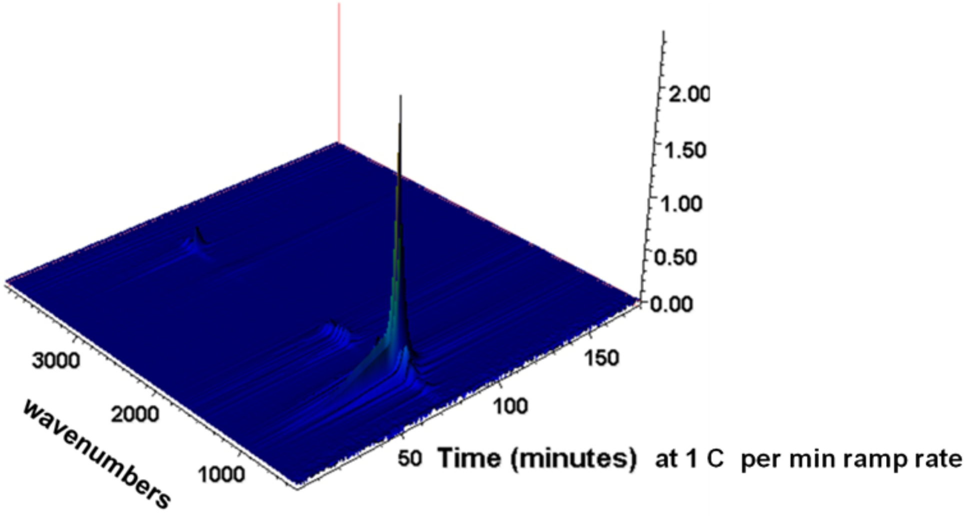
Space group: P1
a= 5.54 Å
b= 7.52 Å
c= 5.36 Å
α= 103.98
β= 64.25
γ= 104.20

Progress with theory for structure prediction.

Predicted structure nearly degenerate with experimental structure (within 11 meV/f.u.)
Predicted structure also has two symmetrically distinct K positions, in agreement with expt.

Metal AB materials





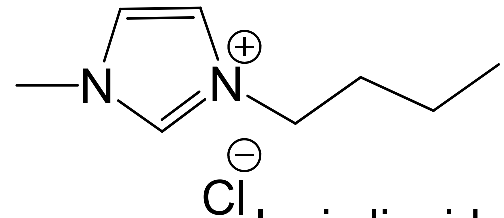
Great kinetics at low temperatures, no borazine, small amounts of ammonia

All materials currently known show exothermic hydrogen release. It is not possible to regenerate these materials efficiently but these materials are useful for stationary near term applications

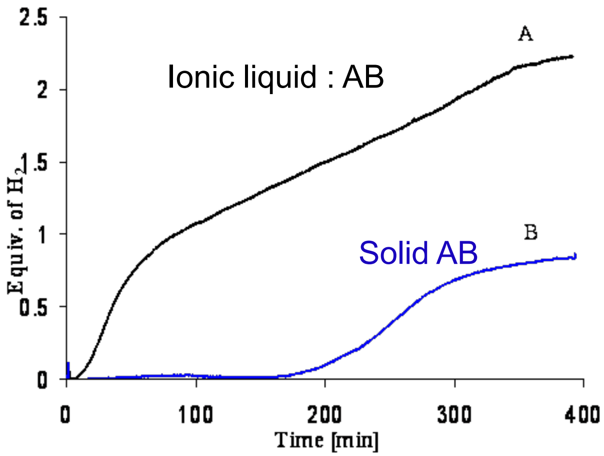
<u>Work with these materials should continue with possibility of better thermodynamics in as yet unknown materials</u>

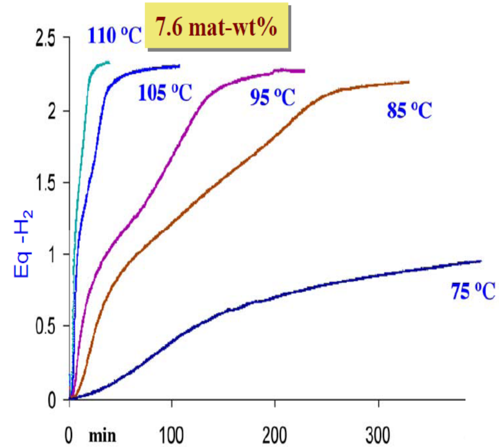
Hydrogen Release from NH_3BH_3 in Ionic Liquids (ILs)

Contrasting dehydrogenation at 85 °C



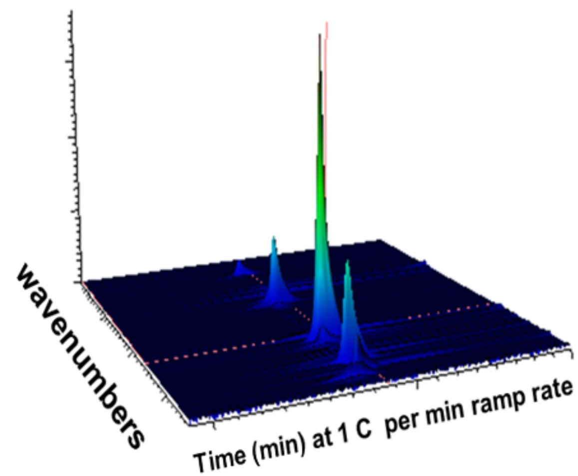
Ionic liquid





Thermal IL release rates AMR 2009 St_16

Penn
University of Pennsylvania

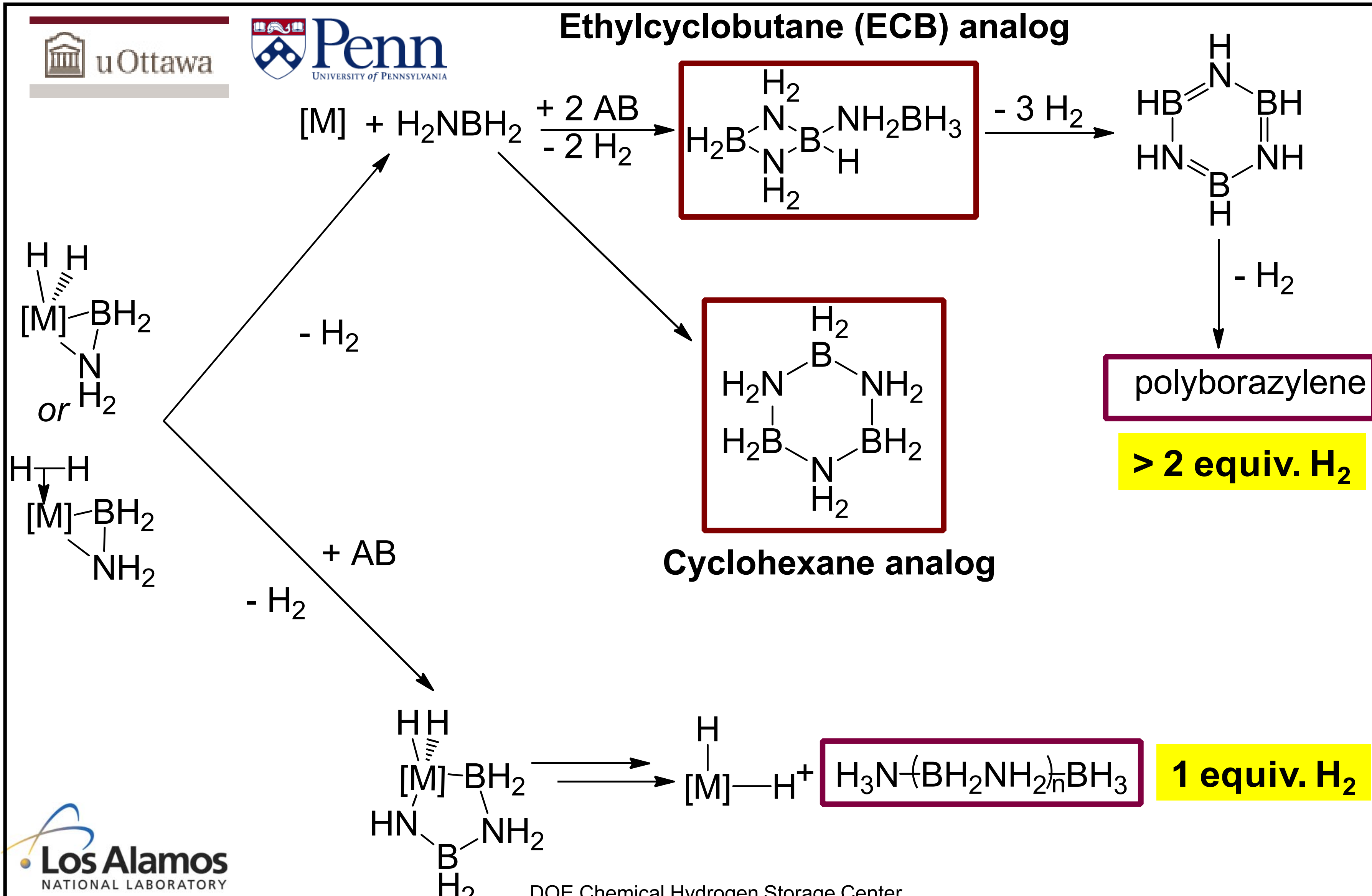


Ionic liquids improve thermal kinetics of hydrogen release

L. G. Sneddon, *et al., J. Am. Chem. Soc.*, **2006**, *128*, 7748.

Impurities still present in hydrogen from thermal release, but no diborane!

2010 Ionic liquids and catalyst results in different reaction products

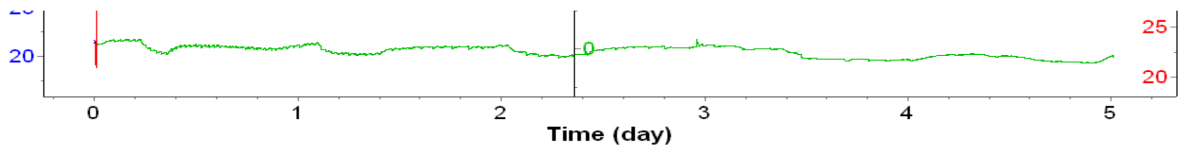


Properties of IL:AB mixtures look promising

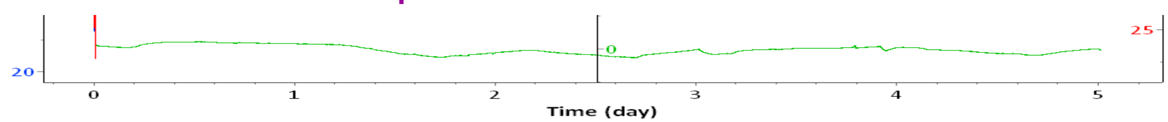
Thermal stability of IL:AB mixtures

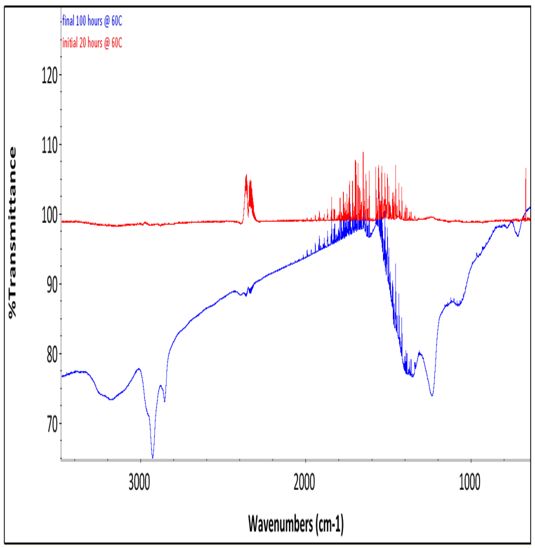
50 ^{o} C - no change on mass of sample or in gas above sample for over 100 hours

50 ^{o} C sample exposed to air - no change on mass of sample or in gas above sample for over 120 hours but water observed in gas. Chloride is hydroscopic



60 ^{o} C sample exposed to air - no change on mass of sample for over 120 hours but slight changes in gas above sample





Only ammonia is observed in the gas phase at 70 C for catalyst but long term stability of samples at 60 ^{o} C still needs to be addressed

Summary – LANL Down Selects for 2010

Organic solvents currently weight % hydrogen too low - stopped

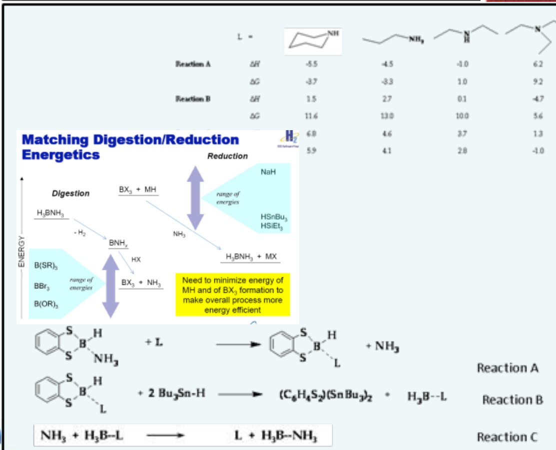
Alkyl ammonia borane materials do not show enough promise, catalyst poisoning and too much impurities in hydrogen to continue – stopped

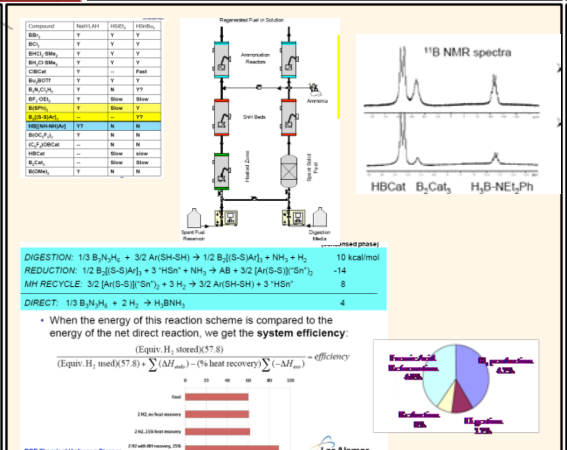
Metal ammonia borane materials have potential but no current material is suitable for automotive applications – small scale continued support

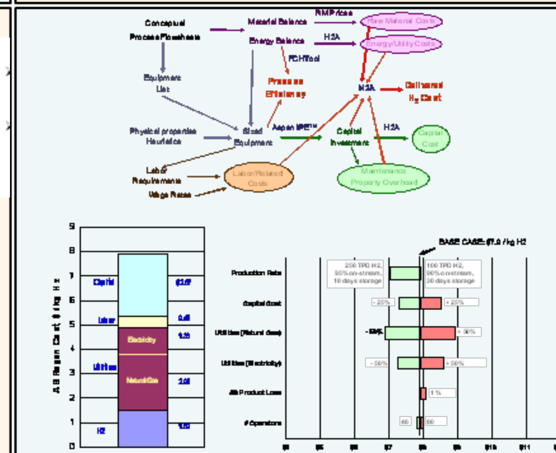
Ionic Liquid systems with catalysts look promising but need to tailor catalyst and ionic liquids combination - continued

Approach - Off-Board Regeneration

2007-08 Discovery	2008 Demonstration	2009-10 Cost Analysis
•Literature search •Theory •Scoping reactions	•Test reactions •Characterization •Scaling •Modeling •Thermodynamic assessment •Feedback to discovery	•Process conceptualization •Flow sheet development •Iterate w/experiments ➢separations ➢kinetics ➢yield •Aspen •H2A Tool







Off-Board Regeneration Required (timeline 2008-2010)

3 Ammonia Borane ($H_3N\text{-}BH_3$) → **Spent fuel** ($B_3N_3H_4$) + $7H_2\uparrow$

$\Delta H \approx$ -7 kcal/mol

(Miranda and Ceder 2007)

2007 – Thiol based digestion of spent fuel first demonstrated

Mid 2007 – Tin hydrides observed to form ammonia borane (AB)

2008 – Digestion/reduction combined into one cycle

Mid 2008 – Feedback from TT, AMR increases emphasis on process analysis, cost; optimization of reactions, reducing unit operations

August 2008 – Center 'Engineering Summit' in Philadelphia with R/H

Fall/Winter 2008/2009 – Iterative process modifications with DOW input;

2010 - DOW analysis of hydrazine regeneration

- Fall 2009 hydrazine Regeneration Scheme
- January 2008 Full Scheme
- Work to DOW Baseline Analysis
- Ultimate Goal

Dow

Argonne NATIONAL LABORATORY

TIAX

Pacific Northwest NATIONAL LABORATORY

Center of Excellence Targets: 60% process efficiency for regeneration
$2-4 gallon of gas equivalent for H_2 stored

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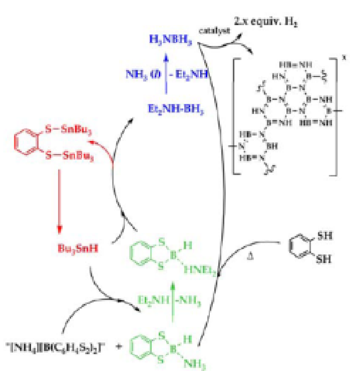
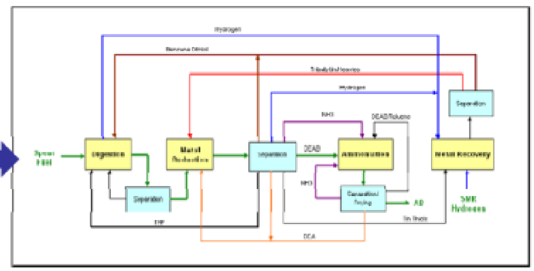
Complete Regen Cycle 3
LANL AMR 2009 (st_17) with cost analysis

Technical Accomplishments and Progress

2009 Lessons Learned from Rohm & Haas Cost Analysis



translates to



2009-2010 Focus Area
Reduce Mass Flow

- •Combine Steps
- •Optimized digestion stoichiometries
- •Optimize amine exchange/ammoniation
- •Consider lower MW reducing agents

ST20

Los Alamos NATIONAL LABORATORY EST. 1943 — DOE Chemical Hydrogen Storage Center — ROHM AND HAAS

Problem: ANL and Dow analysis indicate that SnH reagent too massive and the CO_2 compression was too energy intensive. Significant effort was expended to fix the problems

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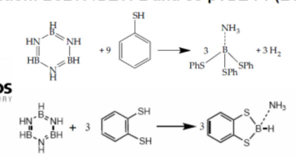
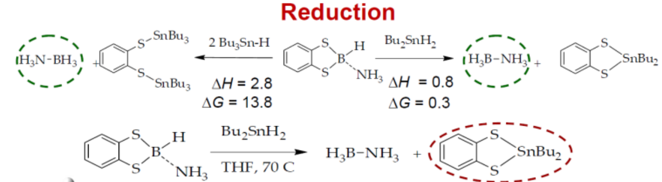
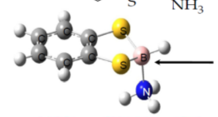
Alternatives to Digestion: S and Sn Compounds (298K)

Reaction: B3LYP/DZVP2 and cc-pVDZ-PP(ECP) for Sn	ΔH	ΔG
	13.1	71.0
• Di-thiol for digestion is better than thiol.	0.5	15.5

Reduction

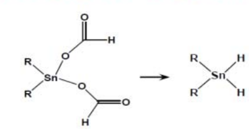


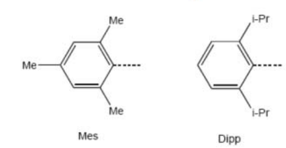


δ_{calc} = -1.8 ppm
δ_{expt} = -5.6 ± 0.2 ppm

- Sn dihydride is a better reductant than monohydride but mono-hydride will work & is commercially available.
- Used for LANL process design. 12

Dihydride Recycle CO_2 extrusion from tin diformates at 298 K in kcal/mol





R	ΔH	ΔG
H	14.6	-4.5
nBu	24.7	5.8
tBu	24.5	3.1
Ph	20.4	-0.6
Mes	18.2	-2.4
Dipp	17.2	-5.7

HOOCH commercial synthesis:

$H_2 + CO_2 \rightarrow H_2O + CO$ ΔH = -0.7
$CO + CH_3OH \rightarrow CH_3O(O)CH$ ΔH = -32.2
$CH_3O(O)CH + H_2O \rightarrow CH_3OH + HO(O)CH$ ΔH = 25.3
ΔH = -7.6

- CO_2 extrusion chemistry favored for free energy due to loss of CO_2.
- Issue is inefficiency of formic acid recycle. Work with LANL to improve the process. 14

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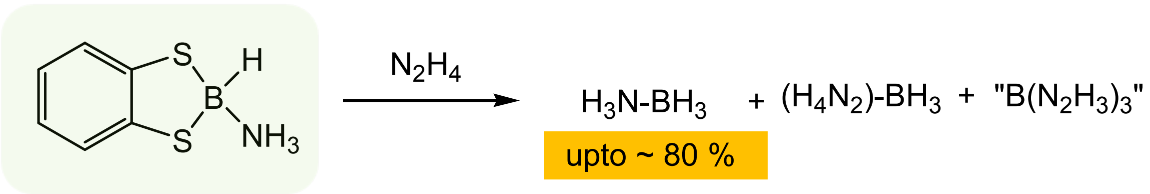
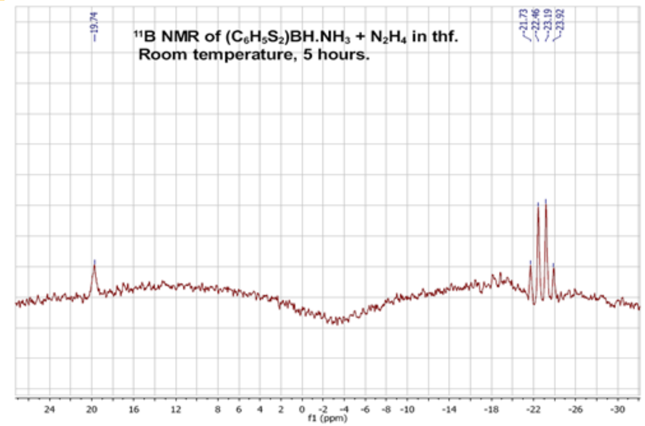
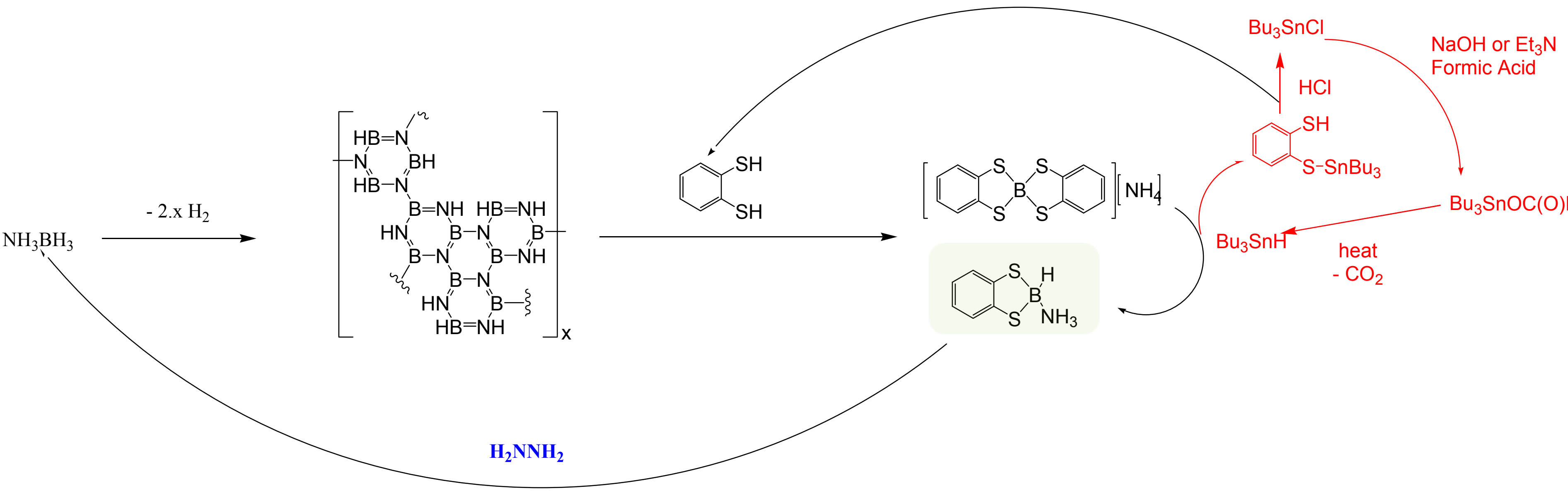
Complete Regen Cycle 4
LANL 2009 (poster)



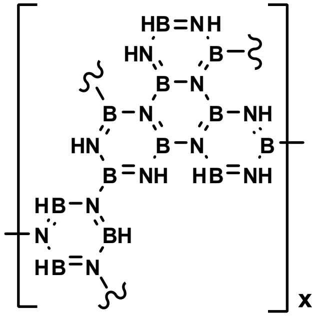




Hydrazine is a light hydrogen transfer material that removed over 50% of weight, due to tin, in the regen cycle. But some tin is still required.

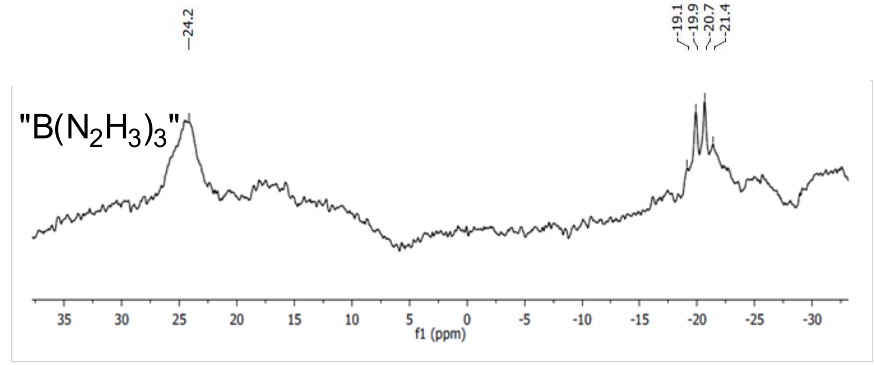
2010 Hydrazine also reacts directly with PB

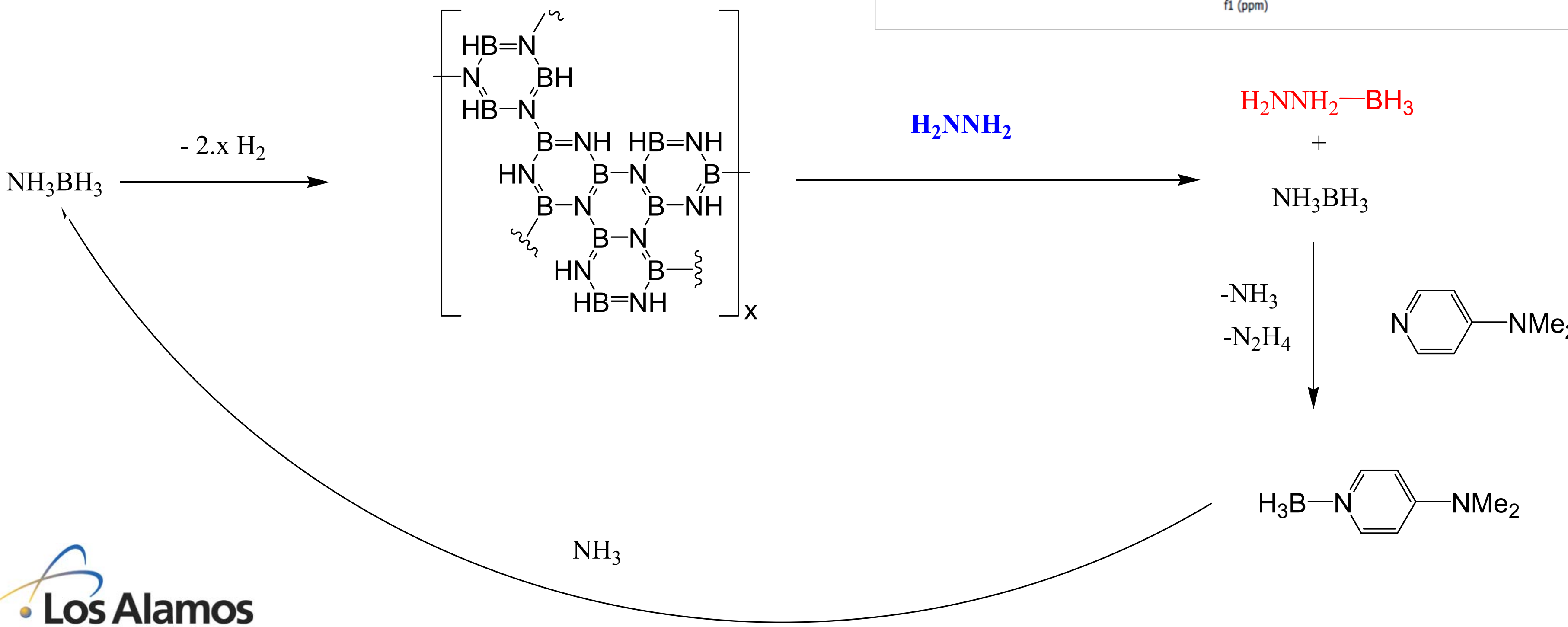
Tin is no longer required but add a amine metathesis step



$\xrightarrow[\text{Heat}]{N_2H_4}$ $H_3N\text{-}BH_3$ + $(H_4N_2)\text{-}BH_3$ + "$B(N_2H_3)_3$"

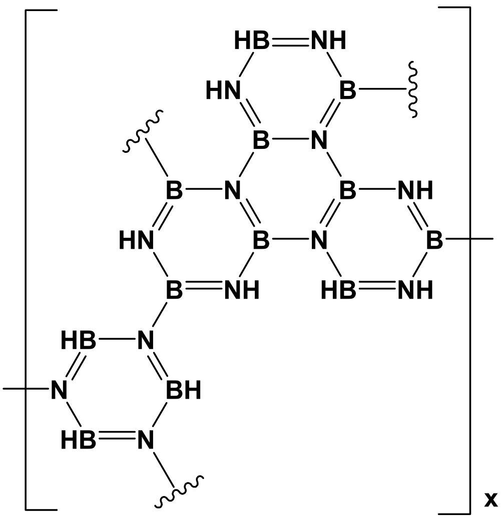
Major Product

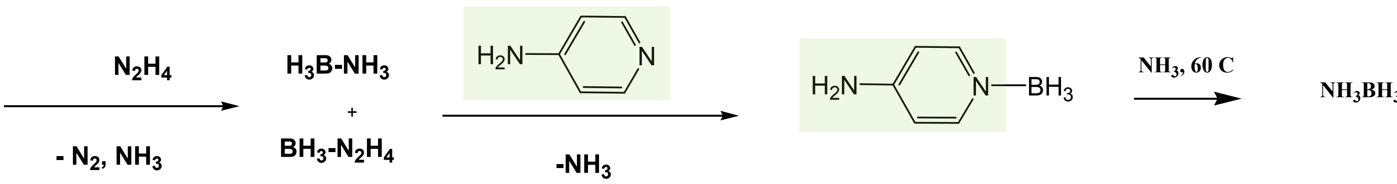




Complete Regen Cycle 5
LANL 2010

Again theory helps select best amine for metathesis





Reactant	B3LYP ΔΔH(rel BDE)		G3MP2 ΔΔH(Rel BDE		B3LYP BDE absolute rel to CCSD(T) NH2NH2		G3MP2 BDE absolute rel to CCSD(T) NH2NH2	
	0K	298K	0K	298K	0K	298K	0K	298K
Ph-NH_2	8.0	8.2	7.0	7.3	39.0	40.4	38.0	39.5
$(C_8H_{18})_3N$	3.0	2.9			34.0	35.1		
Et_3N	3.3	3.0	-1.9	-2.0	34.3	35.2	29.1	30.2
Et_2NH	0.8	0.9	-1.5	-1.5	31.8	33.1	29.5	30.7
EtMeNH	-0.7	-0.6	-2.6	-2.5	30.4	31.6	28.4	29.7
Me_3N	-0.9	-0.8	-4.4	-4.4	30.1	31.4	26.6	27.8
Me_2NH	-1.6	-1.5	-3.3	-3.3	29.5	30.7	27.7	28.9
NH_3	4.7	4.4	6.2	5.9	35.7	36.6	37.2	38.1
Me_2S	9.4	9.8	7.8	8.3	40.4	42.0	38.8	40.5
Et_2S	8.8	9.2	6.9	7.4	39.8	41.4	37.9	39.6
Ph_2S	14.4	14.8	12.1	12.7	45.7	47.0	43.1	44.9
Me_2O	14.5	14.7	13.4	13.8	45.5	46.9	44.4	46.0

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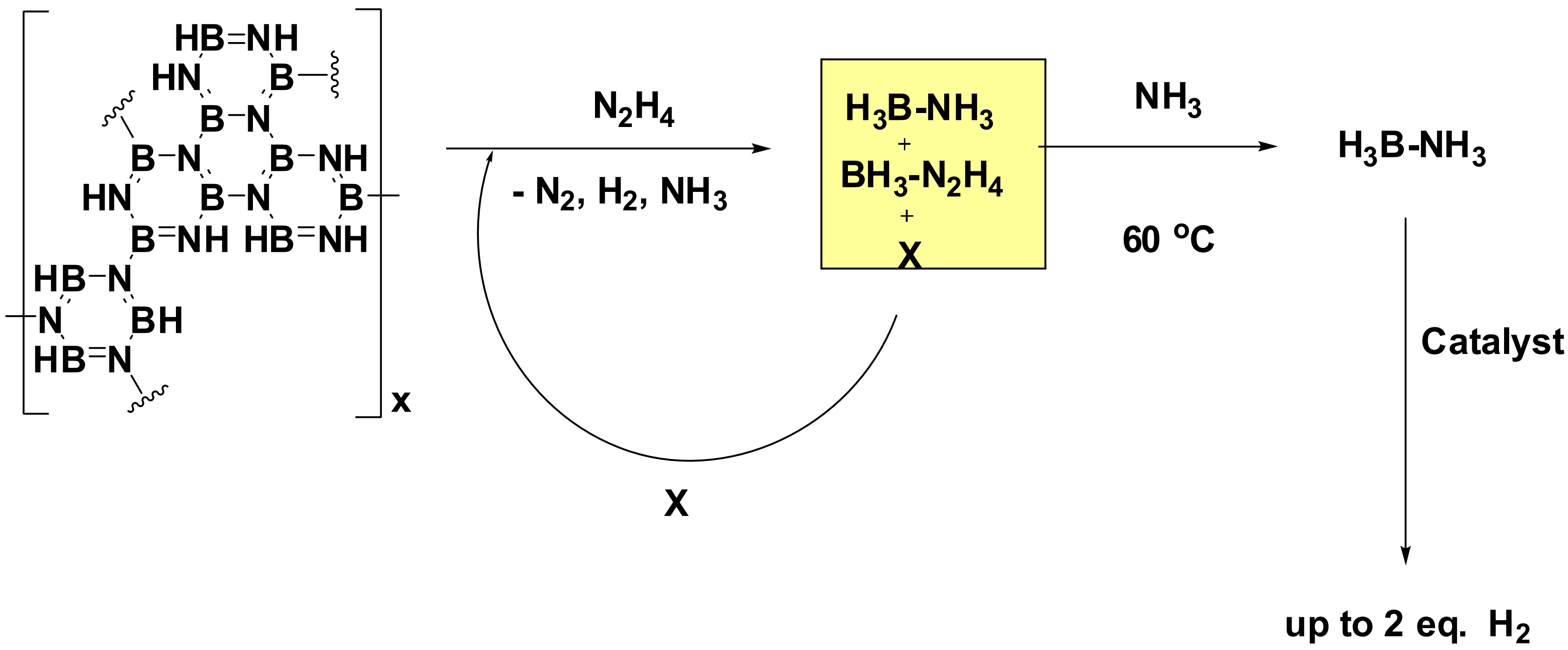
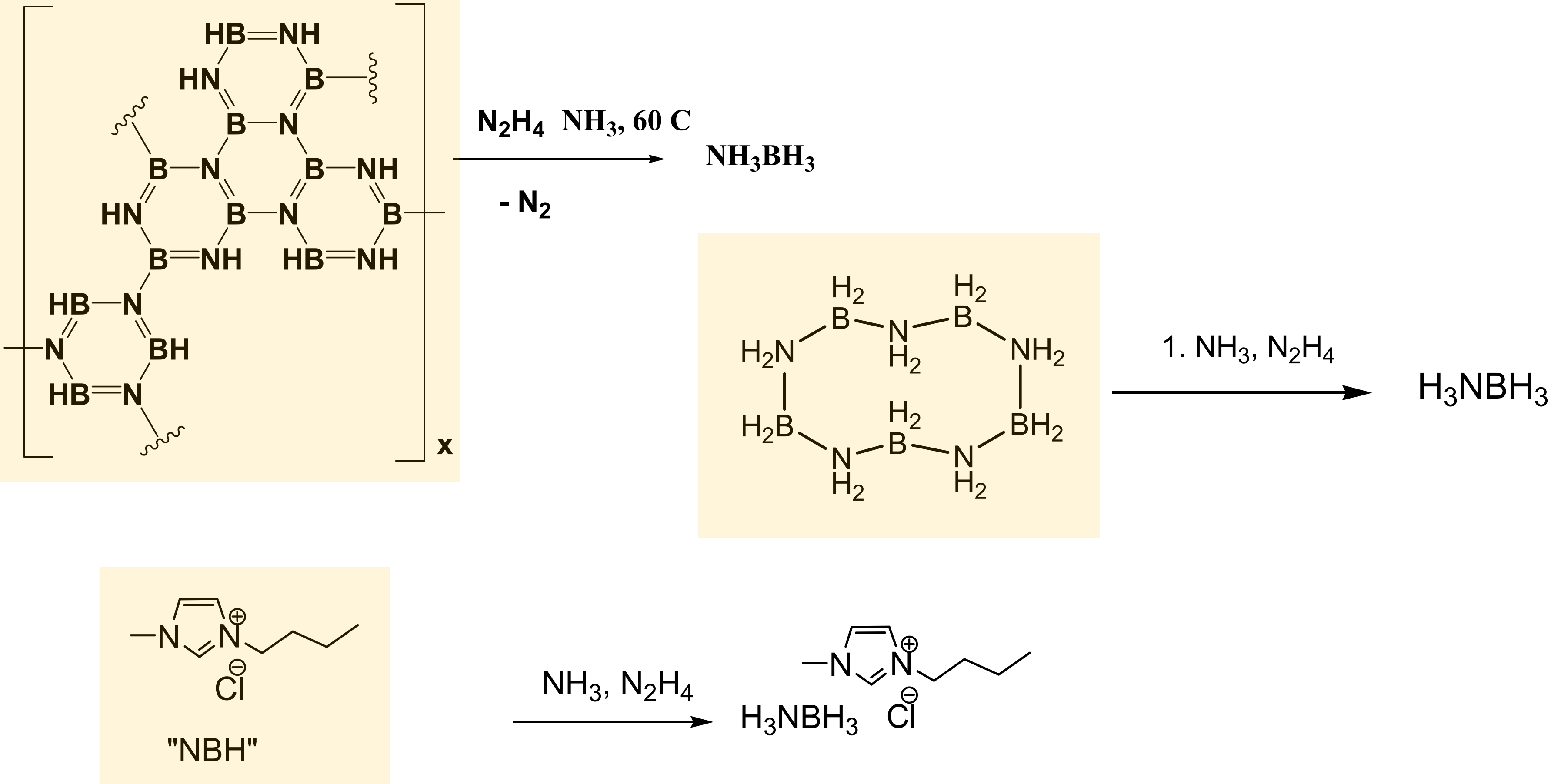
Complete Regen Cycle 6
LANL 2010



At elevated temperature ammonia will directly convert hydrazine borane to ammonia borane

Complete Regen Cycle 7 Demonstrated for several different fuel forms LANL 2010



Ammonia can be used as the solvent in a

one pot direct conversion of spent fuel to ammonia borane

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Summary

To date we have demonstrated 7 complete cycles for regeneration

Regeneration of spent ammonia borane **IS POSSIBLE**

More work is required to determine the optimal regeneration process as both catalysts and fuel form evolves

Current hydrazine synthesis relies on the Chloralkali process, requiring in significant separation (distillation, drying etc) and is therefore expensive!

$$2NH_3 + NaClO \longrightarrow N_2H_4 + NaCl + H_2O$$

Other processes are know in the chemical literature and some are even used commercially but as hydrazine is not used in very large quantities little effort has gone into alternative (cheaper) synthetic routes.

We need to either improve hydrazine cost or develop yet another regen scheme

LANL Materials Comparisons and Progress; Selected Results

Metrics	2005	2006	2007	2008	2009	2010
Grav. density (Mat. wt%)			2007 AB Mixtures	2010 Metal AB's	2010 Liquid AB 2010 Metal AB's	Ionic Liquid ABs Metal AB's
Vol. density (kg-H_2/L)					2010 Liquid AB 2015 Metal AB's	Ionic Liquid ABs Metal AB's
Minimum full flow rate				Platinum catalysts	NON-Platinum catalysts	NON-Platinum catalysts
Operating Temperature				70 ˚C	70 ˚C	70 C
Fuel Purity				inline filter required	inline filter required	inline filter required
Fuel cost					\$7-8 1st process	

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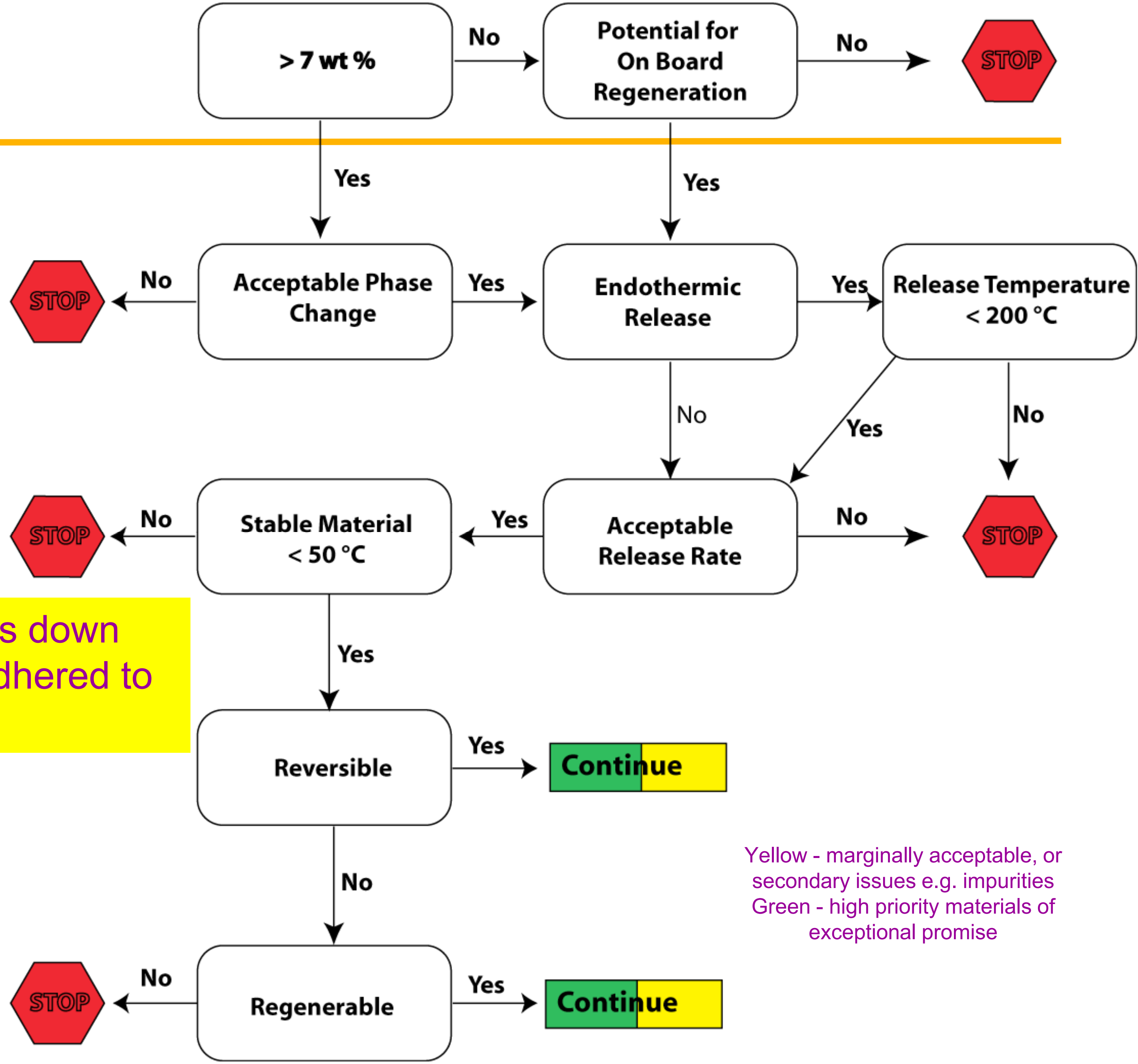
CHSCoE Materials Decision Tree



Criteria for materials down selection has been adhered to by LANL

Yellow - marginally acceptable, or secondary issues e.g. impurities
Green - high priority materials of exceptional promise

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Collaborations

Chemicals COE

- Mizzou – University of Missouri
- Universitas Oregonensis
- Pacific Northwest National Laboratory
- Penn – University of Pennsylvania
- Dow
- 20 Mule Team Borax
- UC Davis – University of California
- The University of Alabama
- University of Washington

IPHE

- IPHE
- The University of Birmingham
- NUS – National University of Singapore
- Industrial Research Limited
- ISIS
- Pacific Northwest National Laboratory
- University of Oxford

Other collaborators:

- uOttawa
- Hiroshima University
- Argonne National Laboratory
- TIAX
- Los Alamos National Laboratory Est. 1943