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

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Project ST 041

Overview

Timeline

- Start 3/2005
- End 9/2010
- 95% Complete

Budget

- FY09: $2350K
- FY10: $1910K

Barriers Addressed

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

Collaborations

Relevance

- **Objectives**
  - Develop materials & methods for low temperature release of pure hydrogen from chemical hydrides with potential to achieve DOE targets
    - **Develop hydrogen release mechanism from MAB**
    - **Focus on quantitative measurements of impurities in H_2.**
  - Demonstrate high efficiency methods for large scale synthesis of chemical hydrogen storage materials
    - **Fabricate reactor to prepare bench scale quantities of ammonia borane.**
  - Develop high efficiency off-board methods for chemical hydride regeneration with potential to achieve DOE targets
  - Support collaborators through expertise in chemistry & characterization to determine the kinetics & thermodynamics of hydrogen release and regeneration of H-storage materials
    - **Work with Center partners to characterize materials and novel approaches to store and release hydrogen.**
- **Impact** Increased assessment of materials and approaches designed to specifically address DOE barriers (volumetric & gravimetric density, H-release rates at low temperatures, H_2 purity, fuel cost and fuel cycle energy efficiency)

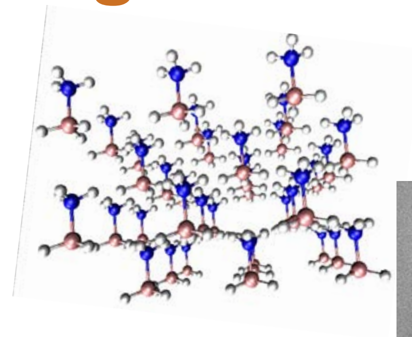
Approach

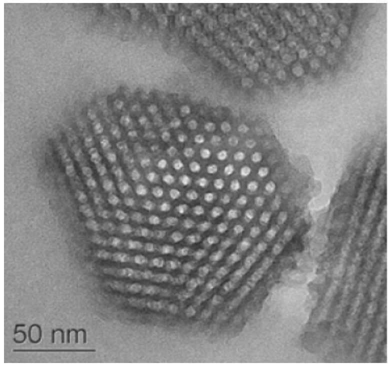
- **Solid State Chemical Hydrogen Storage**
  - Combine experimental & computational approaches with process engineering to develop a mechanistic understanding of H-release from amine boranes, their regeneration from spent fuels, and an understanding of costs.
  - Kinetics and thermodynamic property measurements for hydrogen release and regeneration of spent fuels
  - **Experimental:** NMR and Raman Spectroscopy, XRD, TG/DSC/MS, PCI, Volumetric analysis. Mass spec, NMR, IR, and titration to determine and quantify impurities
  - **Computational:** Electronic structure theory (DFT, MP2 & G3) to understand structural relationships and continuum solvation models to understand solvation effects
  - **Process Engineering:** Engage engineers early to understand costs.

Solid phase chemical hydrogen storage materials studied

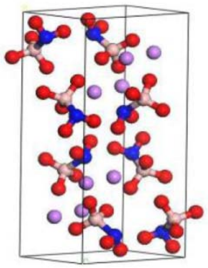
NH_4BH_4	⇔	$BNH_x + H_2$	(240 g H_2/kg, 130 g H_2/l)
NH_3BH_3	⇔	$BNH_x + H_2$	(195 g H_2/kg, 140 g H_2/l)
$[NH_3BH_2NH_3][BH_4]$	⇔	$BNH_x + H_2$	(195 g H_2/kg, 140 g H_2/l)
$LiNH_2BH_3$	⇔	$LiBNH_x + H_2$	(109 g H_2/kg, 52 g H_2/l)
$NaNH_2BH_3$	⇔	$NaBNH_x + H_2$	(76 g H_2/kg , 43 g H_2/l)

PNNL's path of progress through the AB Forest





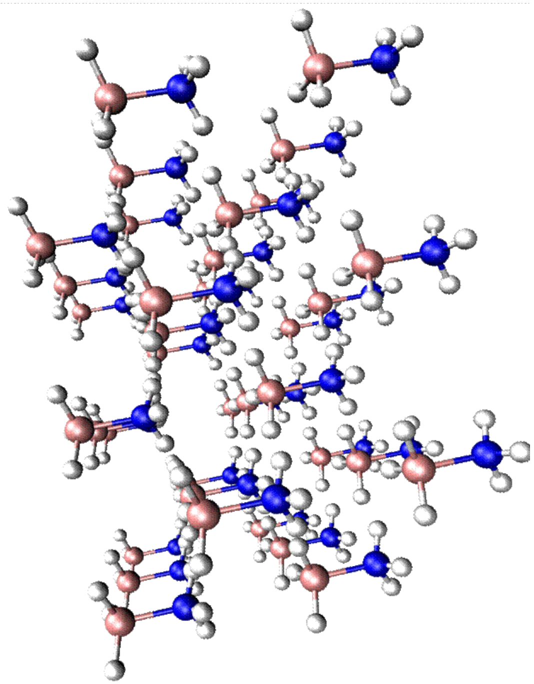
- Started with AB
  - H_2, non toxic, low T release
  - **BUT**- borazine (Bz) release and foam, **SO**…
- Scaffolds – discontinue
  - MCM – discontinue
    - $\downarrow$ Bz, $\downarrow$ foaming, $\downarrow$ T release and $\downarrow$ H_2 content
    - $\uparrow$ AB loading $\downarrow$ stability
  - Carbon and MOF (with Channing) $\downarrow$ stability discontinue
  - BN $\uparrow$ stability, $\uparrow$ Bz discontinue (with UC Davis)
- Additives- **continue**
  - AB release mechanism studies- found additives to improve kinetics
  - AB/MH (with Graetz, Ronnebro) – **continue**
  - AB/$CoCl_2$ (with Chen- IPHE) - $\downarrow$ Bz by 10x! - **continue**
  - AB/cellulose – tested >50 mixtures, eliminated foaming - **continue**



- PNNL started metal amidoborane work and recruited IPHE partners and LANL
- H_2 release mechanisms (with Craig Jensen)
  - AB, DADB, AB+H_2 and MAB **completed**, still working on Bz formation mechanism.
- 1st Fill – single pot AB production developed, studies indicate can be continuous.
- Regeneration - **continue**
  - AB in concentrated solutions for regen- decomposes by 2nd order mechanism
  - Demonstrated steps with Rh – Rh too expensive- discontinue
  - Searching for non-precious metal catalyst system – **continue**
- Increased expert staffing- Abhi Karakamkar, Ewa Ronnebro (IEA), Mark Bowden (IPHE)

Solid Ammonia Borane Key Findings

- **16 H_2 wt%** (material) *usable* gravimetric capacity (system target= 9 wt%)
- **120 gH_2/L** (material) *usable* volumetric capacity (system target= 80 gH_2/L)
- **1.3 gH_2/sec/kg AB** release rate (system target = 0.022 gH_2/sec/kg)
- Stability
  - 50°C for over 90 days with no loss observed
  - Stable in air and water
- Exothermic release 5 kcal/mol H_2 (first equivalent)
- Release temperature – stepwise 90 – 160°C
- Additives- improve performance
  - $CoCl_2$ (IPHE collaboration)
    - <1 wt% borazine
    - 60°C for release on-set – accelerated release
  - Anti-foaming additives demonstrated
- Off-board regeneration steps demonstrated
  - Center demonstrated multiple routes



Recommendation –
Continue Development

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Accomplishments: Milestones FY10

Q3	Complete quantitative analysis of hydrogen purity and kinetics from neat AB
Q3	Complete quantitative analysis of hydrogen purity and kinetics from AB in nano-scaffold materials
Q3	First fill AB production in continuous reactor(s) scheme
Q3	Go/No-go recommendation on chlorinated phenols compatible with Co-H complexes for AB regeneration
Q3	Go/No-go recommendation on fluorinated phenols compatible with Co-H complexes for AB regeneration
Q2	Update flow sheets with regeneration process for Dow to perform high level cost analysis
Q3	Complete Go/No-go recommendation on transition metal amidoboranes, without solvents, composed of TiH_2 mixed with alkali and alkali earth binary hydrides
Q3	Determine feasibility for LiAB regeneration
Q4	Report on hydrogen purity from larger scale (10-100 gram) pellet reactor

Significant PNNL Accomplishments FY10

- *Ammonia borane (AB) first fill reactor capable of 100gram batch*
  - *Provided high purity AB to Center Partners*
- *Metal amidoborane (MAB) release mechanism identified*
- *Quantified impurities in H_2 from AB and demonstrated approaches to mitigate and control*
- *AB + metal hydride mixtures showed different features compared to AB; decreased impurities, less foaming, less exothermic release*
- *Demonstrated >99% boron recovery from digestion of real spent fuels*
- *Identified potential new ammonia synthesis route which may be able to combine first fill and regeneration with potential for lower costs and higher efficiency*
- *Fully characterized spent ammonia borane*
- *13 peer-reviewed publications*
- *Over 45 peer reviewed publications in life of the project*

Accomplishments: Scale-up First Fill Ammonia Borane

- One-pot batch reactor
  - Quantitative (isolated yields ~98%)
  - Purity (^{11}B NMR ~99%)
  - 100 gram batch reactor
  - Demonstrated 20 gram production
  - Provided partners with high purity AB
  - Parametric study indicated semi-flow reactor system possible and provided data for design

Demonstrated 20 gram batch reactor with 100 gram design capacity

Dow's analysis indicated that high purity and yield make PNNL's synthesis superior to State of Art, projected cost $9.1/kg AB

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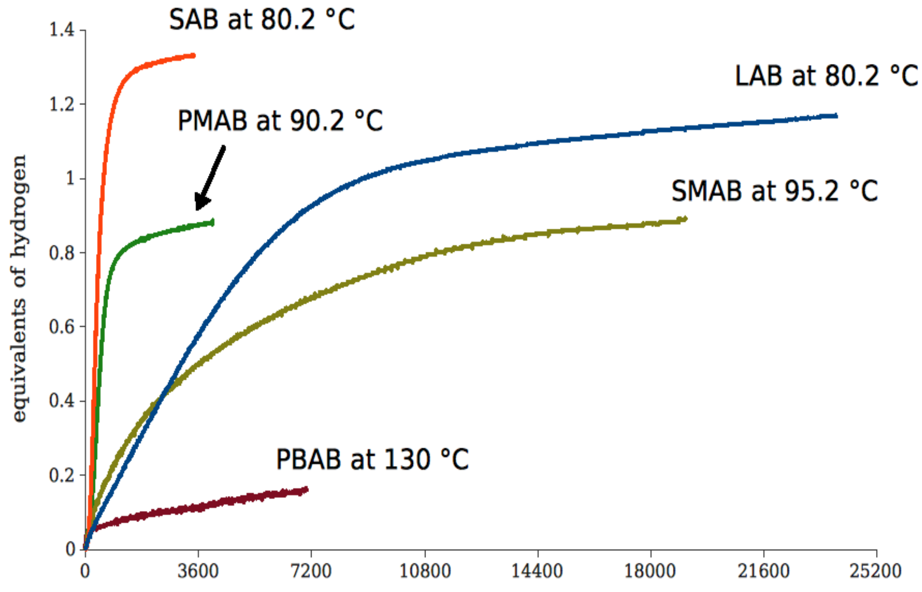
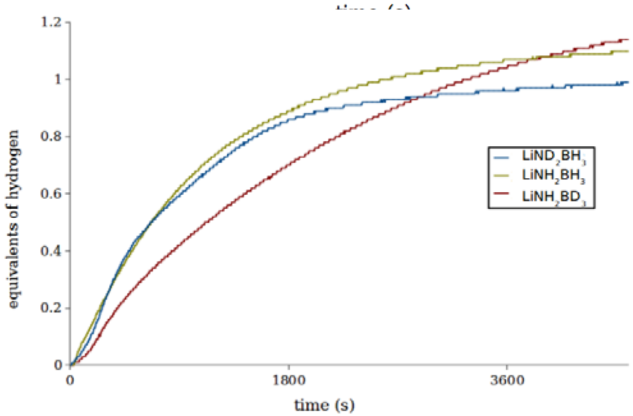
Accomplishment: Metal Amidoborane rate trend for H_2 release from MAB is exact opposite rate trend for H_2 release from Metal borohydrides



Compound		T (°C)	time to 0.5 equiv. H_2 (s)
$LiNH_2BH_3$	LAB	80.2	3070(30)
		85.2	698(8)
		90.2	138(6)
$NaNH_2BH_3$	SAB	70.0	2040(10)
		75.2	684(6)
		80.2	94(2)
$NaNH(Me)BH_3$	SMAB	95.2	3620(84)
		100.2	705(9)
$KNH(Me)BH_3$	PMAB	85.2	992(8)
		90.2	486(6)
$KNH(^tBu)BH_3$	PBAB	130	negligible H_2 observed



The rate trend for release is K > Na > Li
Mechanism is metal assisted hydride transfer
M-N and B-H bond breakage is rate limiting step.

*International Partnership for Hydrogen Economy Project: PNNL, Dalian, RAL, Oxford, IRL, LANL

IPHE

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Accomplishment: Metal Amidoborane

- H_2 release from MAB *completely different mechanism* than AB
  - No "DADB", no induction period, steep temperature dependence
  - No borazine impurity, but slightly higher ammonia.
- Regeneration
  - Using AB regen cycle
    - Need to separate the metal from the B-N
  - Other regeneration cycles not investigated yet
- XAB - new material
  - <6 wt% H_2 (doesn't meet DOE targets)
  - **Endothermic release! – shows possibilities**

MAB produces no borazine
Endothermic release demonstrated
LiAB, NaAB, and KAB discontinued
Work should continue with possibility of better thermodynamics in as yet unknown materials

Accomplishment: Quantitative Direct Impurity Measurement

- Our approach
  - Use multiple analysis tools to quantify Borazine (Bz): NMR, FTIR, Mass spec etc.
  - Develop mechanistic understanding of Bz formation
  - Study effect of H_2 release conditions on concentration
  - Use theory to understand barriers involved
- Experimental set up
  - Use a trap (THF/Glyme) to trap volatile impurities. Use solution NMR to measure.
  - Compare as a function of heating profile
  - FTIR
  - TG-Mass spec/ RGA

Parametric study performed to provide detailed understanding of borazine yields

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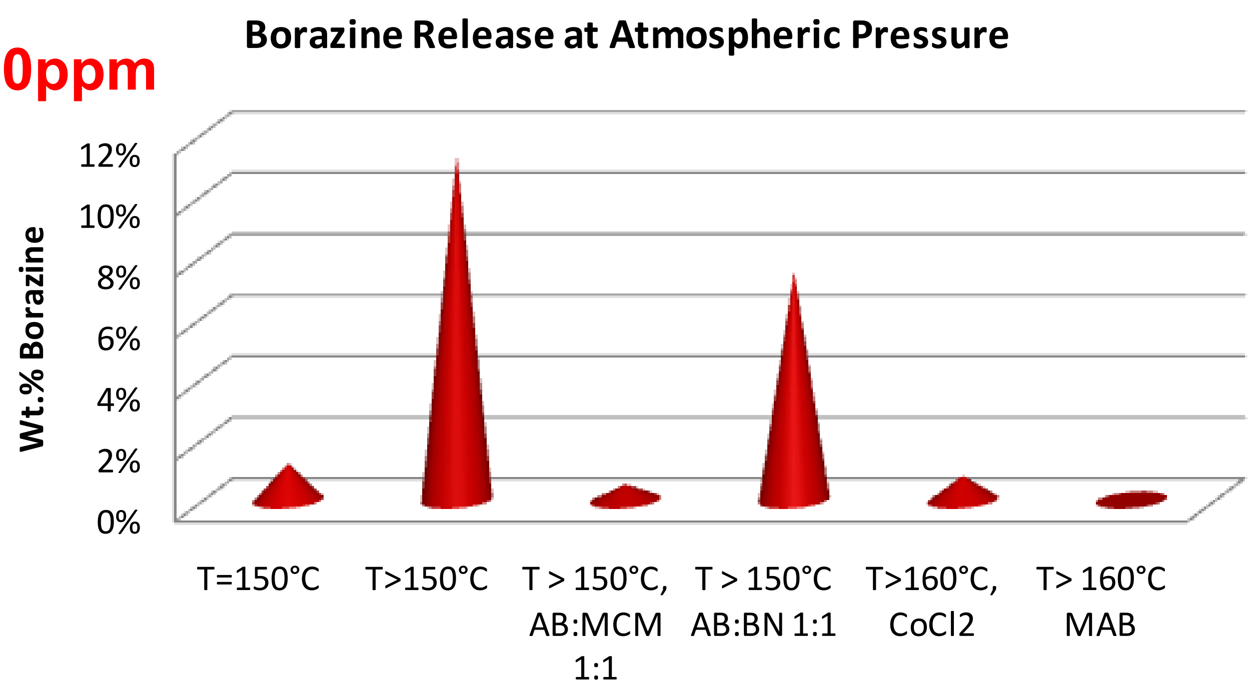
Accomplishment: Ammonia and Borazine Impurity

- Solid AB
  - **Ammonia:100-250ppm**
  - Borazine:
    0.8 wt% - 12 wt%
- MAB
  - Borazine- 0 wt%
  - Ammonia - 0.2 wt%
- Remaining work
  - High pressure
  - No sweep
  - Filters



Catalysts, additives and temperature can control borazine. Ammonia is low

Regeneration Approach: Transition Metal Hydrides to Regenerate AB

- Hydrogen in ammonia borane is polarized … NH_3BH_3
  - Regen spent fuel by addition of H^+ and H^-
- Use transition metal to catalyze heterolysis of H_2

$$H_2 + \text{base} + BX_3 \xrightarrow{L_nM^+} HBX_3^- + H^+\text{base}$$

- Metal complex activates H_2

$$L_nM^+ + H_2 \rightarrow L_nMH_2^+$$

- Base promotes formation of hydride donor, L_nMH

$$L_nMH_2^+ + \text{base} \rightarrow L_nMH + H^+\text{base}$$

- L_nMH transfers H^- to boron

$$L_nMH + BX_3 \rightarrow L_nM^+ + HBX_3^-$$

Accomplishment: Regeneration Scheme Steps Demonstrated with Rh

1) **Digestion**

$BNH_n + 3\ ROH \longrightarrow {}^{n}/_{2}\ H_2\uparrow + NH_3\uparrow + B(OR)_3$

$B(OR)_3 + 3\ PhOH \rightleftharpoons B(OPh)_3 + 3\ ROH\uparrow$

2) **Transition Metal Hydride Formation**

$3\ M^+ + 3\ H_2 \longrightarrow 3\ MH_2^+\ [+\ 3\ base] \longrightarrow 3\ MH + 3\ H^+base$

3) **Hydride Transfer/Ligand Redistribution**

$3\ MH + B(OPh)_3 \longrightarrow 3\ M^+ + HB(OPh)_3^-$

$3\ HB(OPh)_3^- + B(OPh)_3 + Et_3N \longrightarrow 3\ B(OPh)_4^- + Et_3NBH_3$

4) **Recycle**

$B(OPh)_4^- + 3\ H^+base \longrightarrow 3\ PhOH\uparrow + 3\ base + 3\ B(OPh)_3$

5) **Ammoniation**

$Et_3NBH_3 + NH_3 \longrightarrow BH_3NH_3\downarrow + Et_3N$

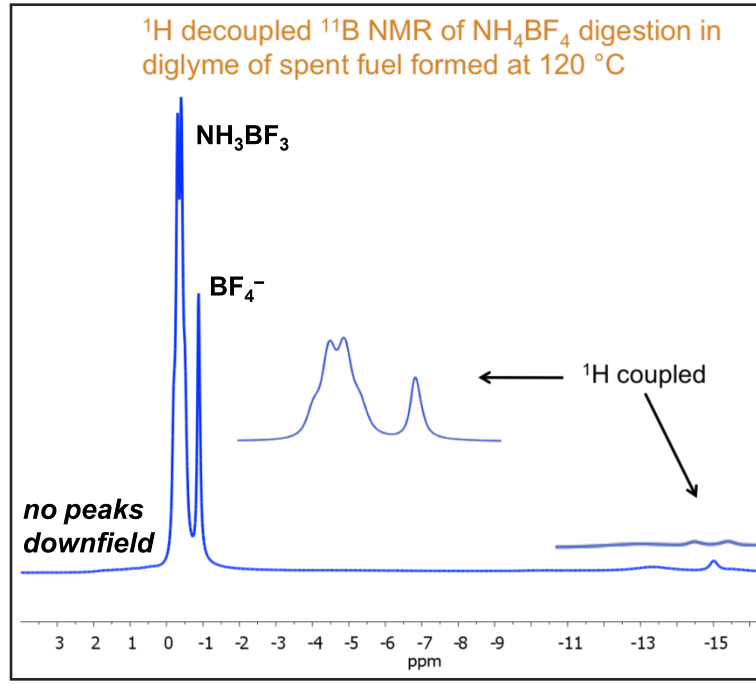
Demonstrated with Rh(dmpe)$_2^+$ and Verkade's super base
… Efforts directed to systems using non-precious metals.
ANL analysis: 22-37% efficiency

Accomplishment: Digestion of spent fuel achieving high B recovery

- Boron recovered:
  - 85% as $B(OEt)_3$ ... still optimizing.
  - white solid bi-product …
    all convertible to $B(OAr)_3$.
  - **>99% B recovery possible**
- New digestion reagent, NH_4BF_4.

$$BNH_x \xrightarrow{NH_4BF_4,\ THF} NH_3BF_3$$

  - "HF" transfer
  - Et_3NBF_3 reduced with RhH
  - potentially lower processing cost



$$4\ Et_3NBF_3 + 3\ (dmpe)_2RhH \xrightarrow{50^o,\ 1h} Et_3NBH_3 + 3\ (dmpe)_2RhBF_4$$

B recovered in high yield
Novel digestion by NH_4BF_4, potential to lower cost

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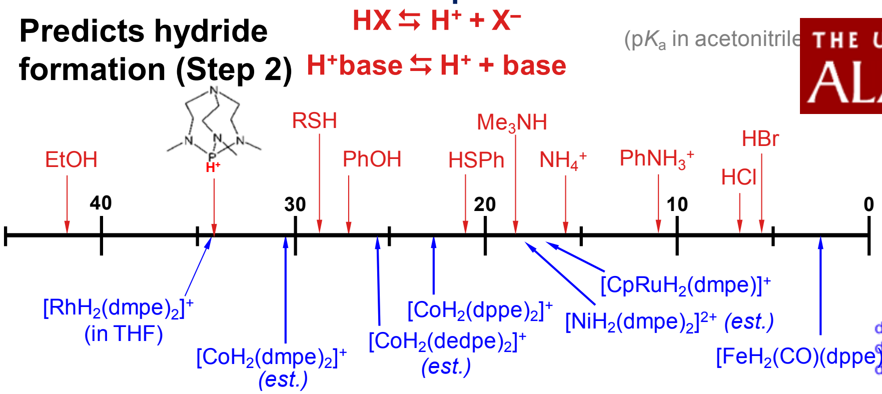
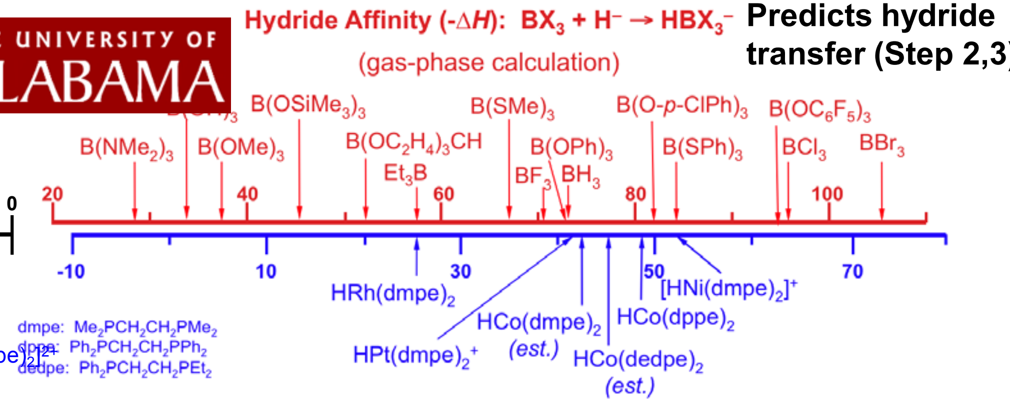
Accomplishment: Co and Ni Catalysts

FY08-FY09 developed and validated tools

Predicts hydride formation (Step 2)



Predicts hydride transfer (Step 2,3)



FY10: Using the tools, identified halogenated phenyl borates for testing with CoH and NiH⁺

Co de-chlorinates chlorophenyl borates – discontinue

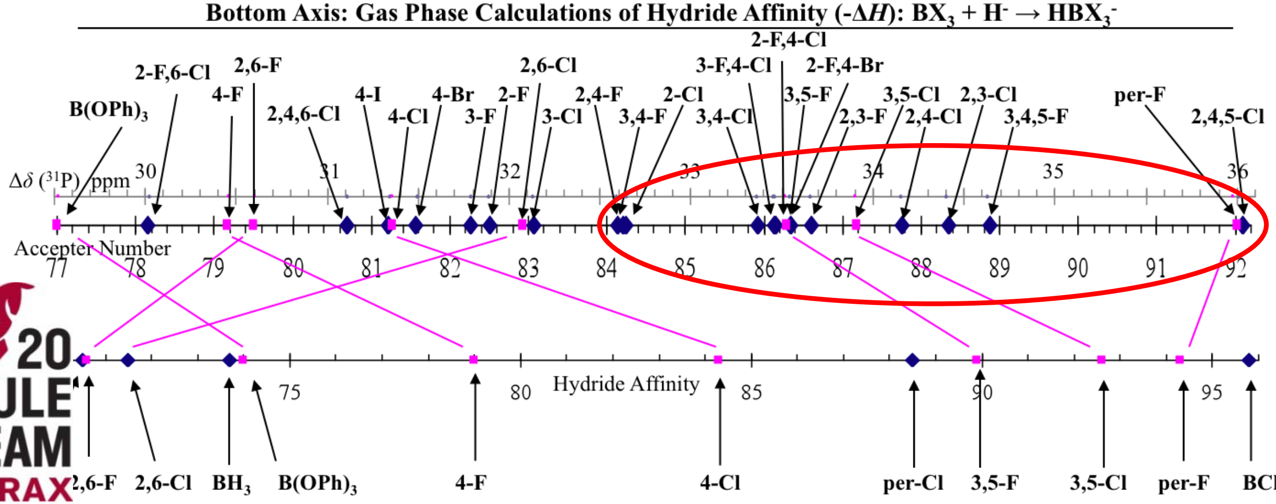
Fluorinated phenyl borates do work with Co - continue

Nickel being evaluated for both Cl and F compounds

Various Et_3PO-$B(OAr)_3$ Adducts:

Top Axis: $\Delta\delta$ ^{31}P ppm **Middle Axis: Gutmann's Accepter Numbers**

Bottom Axis: Gas Phase Calculations of Hydride Affinity (-ΔH): $BX_3 + H^- \rightarrow HBX_3^-$



Lewis Acidity by Substituent:

Identity:	Br > Cl ≥ I > F > H
Quantity:	5 > 3 > 2 > 1 > 0
Position:	2 > 3 > 4

Substitution at Both 2 and 6 Positions:

Cl: hinders Et_3PO coordination as observed for 2,6-Cl and 2,4,6-Cl

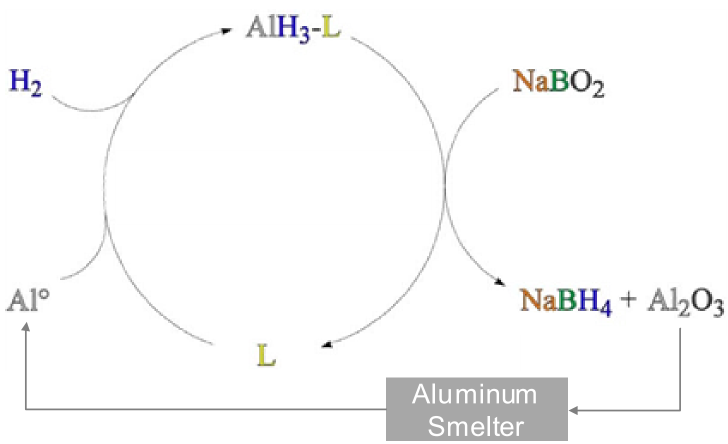
F: effect not as obvious based on data from **per-F ester**

Accomplishment: New 1st Fill Route, Potential new Regen Route

- PNNL 1st fill route produces H_2 as byproduct.

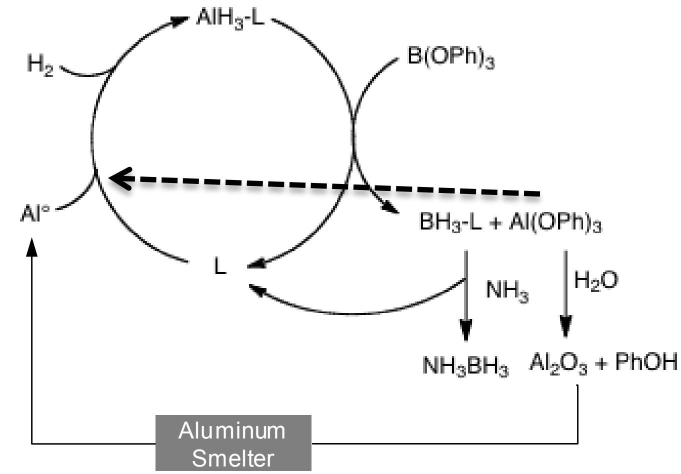
$$NH_4Cl + NaBH_4 \xrightarrow{NH_3/THF} NH_3BH_3 + NaCl + H_2$$

- 25 % efficiency hit.



Low-cost route to $NaBH_4$ (2009 AMR)

- Direct synthesis of R_3NBH_3
  - Avoids inefficiency of using $NaBH_4$
  - Uses Al° more efficiently



$$Al^\circ + H_2 + B(OPh)_3 \xrightarrow[NR_3]{2000psi,\ 180^\circ} R_3NBH_3 + Al(OPh)_3$$

Ashby & Foster (1962)

$$Et_3NBH_3 \xrightarrow{NH_3/THF} NH_3BH_3 + NEt_3$$

PNNL (AMR 2009)

$$EtMe_2NAlH_3 + B(O_2CCF_3)_3 \longrightarrow EtMe_2NBH_3$$

Sneddon (AMR 2007)

$$AlH_3 + B(OPh)_3 \xrightarrow{NEt_3,\ RT} Et_3NBH_3 + Al(OPh)_3$$

96% + 4% Et_3NBH_2OPh

Potential to reduce 1st Fill Cost

Recommend- Direct conversion of Al-OPh to Al-H – we have ideas

Potentially applicable to both Regen and 1st Fill

Summary

Release

- Metal Amidoborane
  - Mechanism determined
  - XAB- endothermic release demonstrated
- Quantified Borazine and Ammonia Impurity
  - Borazine impurity is dependent on temperature
  - Temperature above 160°C increase borazine from <2wt% to 12wt%
  - Additives can decrease borazine at T>160°C (<1wt%)
  - AB ammonia 100-250ppm
  - MAB – 0wt% borazine, 2000ppm ammonia

First fill Ammonia Borane scale up

- 20 g scale demonstrated with potential for 100 g scale
- Parametric studies to understand engineering scale up
- Semi-continuous flow reactor being designed.

Regeneration

- Characterized spent fuel
- Demonstrated regeneration steps
- High boron recovery from real spent fuel digestion
- Novel digestion with NH_4BH_4 - potential to lower cost
- With US Borax, identified possibilities to regen with Co and Ni.
- Identified potential First Fill Route
  - Uses Al° more efficiently and Avoids inefficiency of using $NaBH_4$
  - Less expensive First Fill
- Can we directly go from Al-OPh to Al-H?
  - Potential to combine Regen with First Fill into 1 plant

Accomplishments: Summary Table H_2 Release

compound	gravimetric	volumetric	additive	enthalpy	peak rate	temperature	NH3	Bz	notes	Continue?
	g H2/kg	g H2/l		kJ/mol	g/s/kg	C	ppm	wt%		C/D
NH3BH3	194 (160)	146 (120)	none	-23	1.3	160	100-250	4-12	foams	C
NH3BH3	"	"	none	-23	0.93	145	100-250	2-4	foams	
NH3BH3	"	"	none	-23	0.43	130	100-250	2-4	foams	
NH3BH3 + AF	155 (136)	117 (102)	anti foaming	-23	0.43	130	100-250	2-4	no foam	C
NH3BH3	155	117	$CoCl_2$	?	?	60	?	0.8	no foam	C
AB:MCM	"	"	scaffold (1:1)	-1 (-22)	2.8	130	100-250	<1	no foam	D
AB:MCM	"	"	scaffold (2:1)	-10	?	130	100-250	<1	no foam	D
AB:MCM	"	"	scaffold (3:1)	-12	1.9	130	100-250	<1	no foam	D
DADB	194 (160)	??	none	-16	1.8	145	?	?	little foam	C
DADB	"		none	-16	0.48	130	?	?	little foam	
DADB	"		none	-16	0.2	100	?	?	little foam	
NH4BH4	240	130	none	-63	?	40	?	?	little foam	C
LiNH2BH3	109	52	none	?	1.76	130	200	0	no foam	D
LiNH2BH3	"	"	None	?	0.44	100	2000	0	no foam	
LiNH2BH3	"	"	None	-2	0.08	90	2000	0	no foam	
LiNH2BH3	"	"	None		0.01	80	2000	0	no foam	
NaNH2BH3	76	43	none	?	0.044	80	?	0	no foam	D
NaMeNHBH3	30	??	none	?	0.043	100	?	0	no foam	D
$KNH(Me)BH_3$	20	?	none	?	?	85	?	0	no foam	D
$KNH(^tBu)BH_3$	15	?	none	?	?	130	?	0	no foam	D

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. All compositions tested are not shown. C= Continue, D = Discontinue for on or off board transportation systems, still may be applicable for stationary or portable applications

Collaborative Activities

Chemical Hydrogen Storage Center of Excellence	• UCD - study AB on nanoBN • Penn - NMR and calorimetry support to Penn • UW - measure ΔH for catalytic AB • UO - measure ΔH for CBN compounds • Dow - develop cost est. for 1st fill & regen • Alabama - develop solvation models & benchmarking thermochemistry • USB - characterize novel BX_3 esters
IPHE	• Dalian Institute of Chemical Physics (China), Industrial Research Limited (New Zealand), Rutherford Appleton Laboratory (UK), Oxford (UK), LANL - study properties of metal amido boranes
Independent Projects	• H2 Tech - best practices for chemical hydrides
Materials 'Reactivity' Program	• Dedrick (SNL) and Anton (SRNL) - understand reactivity properties of AB • Dedrick - study impurities in H_2
Independent Analysis	• Dow and Alabama with ANL and TIAX - provide parameters for regen cost and efficiency analysis

Future Work – Center Ends FY10
Remaining issues / recommendations

- AB 1st fill
  - Batch to continuous reactor approaches
- Solid forms
  - Enhance H_2 purity
    - Reduce or avoid borazine formation (preliminary results for additives promising)
    - Impact of increased pressure
    - Spent fuel as a borazine filter
  - Fuel blends (AB mixed with other H-storage materials)
  - Heat/mass transfer effects in pellets (exothermic kinetic benefit)
- Regeneration
  - Complete transition metal regeneration candidate screening
  - Optimize the process steps
  - New first fill cycle evaluation
    - Direct conversion of Al-OPh to Al-H: enable Regen and 1st Fill
  - Regeneration of MAB, and AB+Metal hydride mixtures

Abhi Karkamkar, Avery Luedtke, John Linehan, Wendy Shaw, Richard Zheng, Daiwon Choi, Chris Sorensen, Tricia Smurthwaite, David Heldebrant, Scot Rassat, Chris Aardahl, Don Camaioni, Michael Mock, Robert Potter, Dan Dubois, Jun Li, Jerry Birnbaum, Richard Zheng, John Linehan, Suh-Jane Lee, Ken Rappè, David Rector, Tom Autrey, Dean Matson, Ewa Rönnebro, Jamie Holladay, Mark Bowden, Doinita Neiner

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Extra Slides

- Post project transition
- Publications
- Presentations
- Response to reviewer comments
- Lessons learned, a partial list
- Preliminary regen efficiency analysis (ANL)
- Characterization of spent fuel
- Summary of PNNL's accomplishments FY06 to FY09

Post Project Transition

- Project due to end March 2010
- Final report will be submitted to DOE with recommendations for future research in chemical hydrogen storage materials
  - Materials
  - Regeneration schemes
- Hand off of properties information to Engineering CoE and other relevant DOE projects

Lesson's Learned*

- Pro's to Center Concept and Structure
  - Common platform for interactions
    - Need to have solid IP agreements and NDA's
    - Need respectful, but frank discussions.
  - Facilitated the creative process through open discussions workshops
  - Faster progress through spreading the work around and having access to more resources
  - 5 yr funding provides stability for academic partners to attract the best students and national laboratories to attract and retain the best scientists and post docs.
  - Center partnership instilled high performance standards
- Cons
  - Very difficult to add new partners
  - Very difficult to remove underperforming partners
  - Very difficult to look at new ideas that are on the edge of the Center's area
  - Certain partners take things very seriously and are responsive….others not so much. This may be the same for a collection of separate projects.

*This is just a brief summary. More in depth lesson's learned will be in the final report.

Lesson's Learned*

- Must haves
  - TRUST- all Center partners must respect the other partners and not "stab them in the back". For example, before negative information about one Partner's research or area is communicated, all partners should discuss with that partner what is being communicated and how to give them a chance to respond.
  - IP rights must be respected. Even the appearance of "stealing of ideas" will destroys trust which is a key for Center success.
  - Diverse team- theorists, experimentalists, and industry ALL giving input
  - Engage engineers/industry early and often, and use their input.
  - Strong Center Lead(s)
    - Must ensure communication between the labs
    - Must be able to keep the participants focused on the ultimate goals. It is easy to get parochial and/or side tracked.
    - Must be able to keep a level head and smooth things over when "bumps" occur
    - Must be able to kill off technologies that won't work. It helps to be able to redirect the investigators to other areas.
  - Strong support from DOE TDM's, who work with the Center leads and partners in directing the work.

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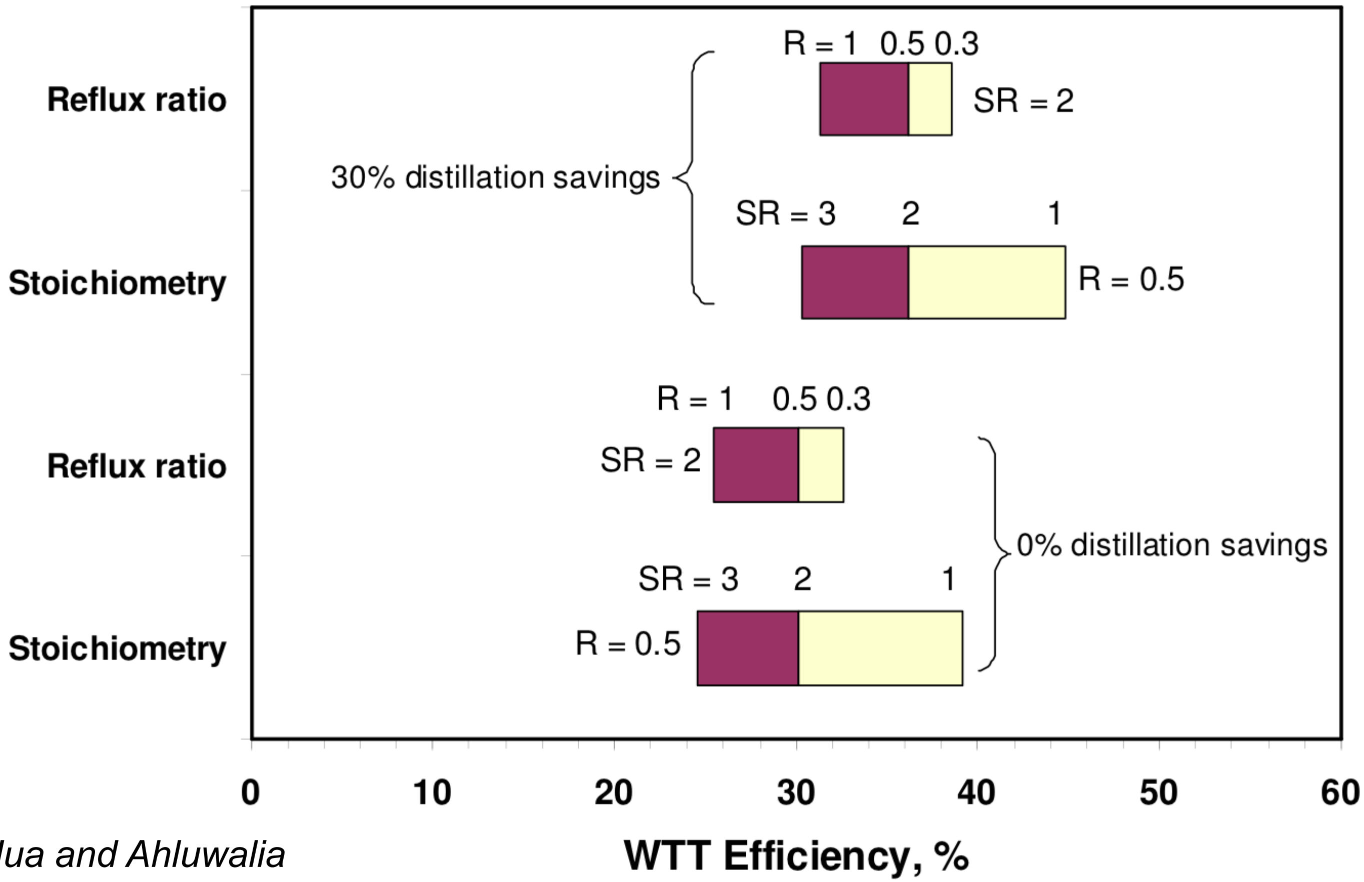
ANL performed energy and efficiency analysis

- Two approaches for digesting spent fuel to $B(OPh)_3$ and NH_3 were considered.
  - Convert residual B-H to H_2.
  - Preserve residual B-H bonds in $(BHNH)_n$.
- Preliminary estimate of well-to-tank efficiency is 25-47%.
  - Base and transition metal complex undefined.
  - Energy for separations in recycle of $B(OPh)_4^-$ not included.
- Approach that preserves residual B-H is ~10% more efficient.
- Analysis will be performed to determine dependence of efficiency on residual H in spent fuel, i.e., "n" in BNH_n.

Process efficiency sensitive to stoichiometries, separations and heat integration

FCHtool Analysis: Well-To-Tank Efficiency



Analysis for scheme that preserves B-H in spent fuel

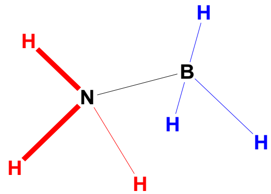
Hua and Ahluwalia

Argonne NATIONAL LABORATORY

10

Pacific Northwest NATIONAL LABORATORY

Characterization of spent fuel



150 ºC

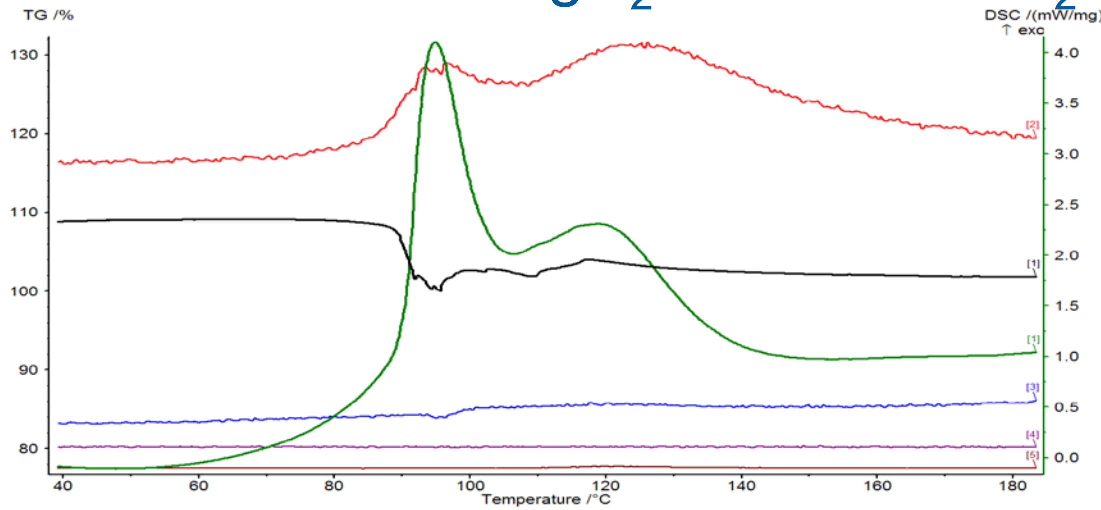
BORAX

- Prepared from gram quantities of AB
  - Heated in Parr reactor for 3 hours at 150 °C (>200 psi); cooled to 25° and flu gas vented.
  - Heated in burette system 150 °C till >2 equiv. of H_2 evolved.
- Elemental analysis and hydridic hydrogen content of spent fuel determined by US Borax.
  - Nitrogen is present in excess of boron
  - More NH than BH
- Boron content (~39 %) used to calculated yield of digestion yields.

Ammonia borane (AB) and metal hydrides -new combinations at PNNL

- Candidates
  - AB + Mg
  - AB + CaH_2
  - AB + TiH_2
  - AB + MgH_2 + TiH_2
  - AB + $Mg(BH_4)_2$
  - AB + $Ca(BH_4)_2$
- MBH_4+AB detailed analysis underway
  - Isothermal
  - Enthalpies / activation energy
  - Molar ratio effect on properties

AB + 50 mole% MgH_2+ 10mol% TiH_2



- 7.3 H_2 wt%
- Thermal features similar to AB ‘as is’
- Release T = 88°C
- Almost no borazine or ammonia
- Much less foaming
- Less exothermic H-release observed

New features were observed – decreased borazine and foaming

Regeneration using current schemes would require separation of the metals

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

Summary of Major Achievements in FY 05 and 06

- FY05- beginning of project
  - Ammonia borane studies begun
  - Computations show potentially high storage capacity
  - Synthesis of scaffolds of varying pore diameters
  - Flowsheets and completed for “model” systems

- FY06
  - Multi-scale models developed
  - Increased thermochemistry understanding
  - “Seeding” of ammonia with partially spent AB to accelerate release demonstrated
  - AB on scaffolds demonstrated

Summary of Major Achievements in FY 07

- Release
  - Developed understanding of mechanism for H_2 release from AB
  - Identified additives that accelerate release
  - Shown AB stability at 50/60°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 requirements on reactor dimensions
  - Preliminary consideration of fuel morphology indicates capacity targets likely within reach

Summary of Major Achievements in FY 08

- Release
  - Developed Li-NH_2–BH_3 under IPHE collaboration: increased H_2 release kinetics by order of magnitude
  - Discovered additives that suppressed foaming
- Regeneration
  - Demonstrated hydride transfer Chemistry from activated H_2 to spent fuel.
  - Theoretical calculations now point to energy efficienct regeneration apporach with non-PGM reduction pathway: reduced fuel cycle costs
  - Preliminary flow sheets for regeneration enables identification of process knowledge gaps.

Summary Accomplishments FY09

Release …*focus on stability, solid fuel forms and H_2 purity*

- Stability of AB and NH_4BH_4 … short shelf life AB in solution. NH_4BH_4 stable at room temperature
- Additives… fibrous compounds preserve solid fuel morphology)
- Purity of H_2 … ammonia (100-200 ppm) and borazine (~4wt%) independent of heating rate
- Metal amido boranes (LiAB) … high rates at low temperatures but stable at moderate temperatures

First fill AB Scale up

- Batch reactor to prepare AB (98/99). Minimize separations
- 10 g scale demonstrated, 100 g scale reactor next

Summary Accomplishments FY09

Regeneration … *developed a process for regenerating AB from H_2 and demonstrated individual steps.*

- Demonstrated H_2 activation with cobalt complex and conversion to $(diphos)_2CoH$ with base
- Demonstrated H^- transfer to digested fuel targets (BX_3) from $(diphos)_2CoH$ … readily generated with H_2 and base

- Collaborated with ANL to obtain preliminary estimate of energy efficiency for approaches that digest spent fuel to $B(OPh)_3$ and NH_3.
  - Convert residual B-H to H_2.
  - Preserve residual B-H bonds in $(BHNH)_n$.
  - Preliminary estimate of well-to-tank efficiency is 25-47%.
  - Base and transition metal complex undefined.
  - Energy for separations in recycle of $B(OPh)_4^-$ not included.
  - Approach that preserves residual B-H is ~10% more efficient.

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